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AN EVALUATION OF POLYCYCLIC AROMATIC HYDROCARBON EXPOSURE FROM VEGETATION GROWN IN CONTAMINATED SOILS

BY

RAMAN BIRK

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE**

IN

ENVIRONMENTAL SCIENCE

DEPARTMENT OF CIVIL ENGINEERING

EDMONTON, ALBERTA

SPRING 1994

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DEDICATED TO MY PARENTS

FOR THEIR LOVING SUPPORT AND INVALUABLE GUIDANCE

ABSTRACT

A health risk assessment performed for a site contaminated by a former petroleum processing facility had identified consumption of vegetation grown in soil contaminated by polycyclic aromatic hydrocarbons (PAHs) to be major route of exposure. Consequently, PAH uptake by three types of vegetation was evaluated in growth experiments, namely: carrots (*Daucus carota*), lettuce (*Lactuca sativa*) and barley (*Hordeum vulgare*). Greenhouse experiments were used to study the uptake from soils amended with creosote, while on-site growth experiments allowed the study of uptake from the abandoned Borradaile oil refinery site. In both experiments, three exposure pathways were considered: particulate deposition, vapor transfer and root uptake.

For the particular experimental conditions used the dominant route of PAH exposure was volatilization from the soil to the foliage, with the low molecular weight PAH compounds (3 and 4 rings) dominating individual components of the total PAH load. Lettuce accumulated higher levels of PAHs than barley and carrots, under the treatment where the plants were exposed to the soil surface. This was explained as a result of the broader leaves and growing at ground level, allowing a greater surface area for entrapment of the volatile and semi-volatile PAHs. The PAH concentrations detected in the carrot root peels were substantially higher than in the core, suggesting little transfer from the peel to the core. Approximately 70 to 80% of the PAH burden found in the carrots was associated with the peel.

In the evaluation the Borradaile human health risk assessment, experimental vegetation and authentic soil data collected from the site were input into dose estimate models and compared to previously estimated values used in the assessment. The authentic and experimental data collected from the site produced a field estimate case two orders of magnitude lower than the base case estimated by the original risk assessment. The analysis

of on-site native vegetation was found to provide another useful comparison for the estimated values that required many assumptions. These results show the value of having analytical data obtained from a site to allow for a more realistic judgement of the possible exposure and corresponding risk from contaminants.

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To the Banff and LH gang - let's shoot a few.

If you see purity
As immaturity
Well it's no surprise
If for kindness
You substitute blindness
Please open your eyes

Table of Contents

Page

CHAPTER 1 Introduction

1.0 INTRODUCTION 1

1.1 Background and Problem Statement 1
1.2 Objectives 2
1.3 Overall Approach 3
1.4 Polycyclic Aromatic Hydrocarbons 3
1.5 Plant Model Structure 7
1.6 Water and Nutrient Movement 11
1.7 Chemical Uptake in the Plant 14
1.8 Plant Uptake Correlations 16
1.9 Uptake Models 25
1.10 Experimental Designs and their Uncertainties 26

1.11 BIBLIOGRAPHY 30

CHAPTER 2 An Investigation of Vegetative Uptake of Polycyclic Aromatic Hydrocarbons

2.0 INTRODUCTION 36

2.1 METHODS AND MATERIALS 38

2.1.1 Creosote Contaminated Soil Greenhouse Experiment 38
2.1.1.1 Experimental Design 38
2.1.2 Borradaile On-site Growth Experiment 43
2.1.2.1 Experimental Design 47
2.1.3 Sample Collection and Preparation 49
2.1.4 Analytical Methods 50
2.1.4.1 Soil Sample Extraction and Cleanup 50
2.1.4.2 Plant Sample Extraction and Cleanup 51

Page

2.1.4.3 Air Monitoring 53
2.1.4.4 Oil and Grease (Solvent Extractable Residue) 55
2.1.4.5 Instrumentation - Thermal Desorption/Gas Chromatography/ Mass Spectrometry and Gas Chromatography/Mass Spectrometry 56
2.1.4.5.1 Thermal Desorption 56
2.1.4.5.2 Gas Chromatography/Mass Spectrometry 56

2.2 RESULTS AND DISCUSSION 58

2.3 CONCLUSIONS 122

2.3 BIBLIOGRAPHY 125

CHAPTER 3 A Risk Assessment Evaluation of Polycyclic Aromatic Hydrocarbon Chronic Dose Exposures at the Borradaile Refinery Site

3.0 INTRODUCTION 130

3.1 METHODS AND MATERIALS 137

3.2 RESULTS AND DISCUSSION 138

3.3 CONCLUSIONS 175

3.4 BIBLIOGRAPHY 176

CHAPTER 4 Summary of Conclusions

4.0 SUMMARY OF CONCLUSIONS 180

Page

APPENDIX A 184

APPENDIX B 191

APPENDIX C 194

APPENDIX D 199

List of Tables

		Page
Table 1.1	PAH Ring Arrangement and Relative Stability	4
Table 1.2	Structures and Physical-Chemical Properties of PAHs	5
Table 2.1	Creosote Contaminated Soil Greenhouse Experimental Design	41
Table 2.2	Borradaile Field Experimental Design	48
Table 2.3	Soxhlet Extraction and Thermal Desorption Recoveries of Two Standard NRC Reference Sediments	60
Table 2.4	PAH Analysis of Borradaile Vegetation by TD/GC/MS	61
Table 2.5	PAH Analysis of Borradaile Soil by TD/GC/MS	62
Table 2.6	PAH Analysis of Borradaile Vegetation by GC/MS-Soxhlet Extraction	63
Table 2.7	Oil and Grease Content of Creosote Contaminated Soil Greenhouse Experiment	65
Table 2.8	Initial PAH Concentrations of Creosote Contaminated Soil at each Dilution	66
Table 2.9	Final PAH Concentrations of Creosote Contaminated Soil at each Dilution	67
Table 2.10	Creosote PAH Levels at Bottom of Treatment Boxes - Leaching	79
Table 2.11	Barley and Lettuce Yields	82
Table 2.12	Carrot Yields	83

		Page
Table 2.13	Abbreviation of Variables and Expected Exposures	85
Table 2.14	Barley Grown in 100%, 50%, 15%, 1% and Control Creosote Levels	86
Table 2.15	Lettuce Grown in 15%, 1% and Control Creosote Levels	90
Table 2.16	Potential for Uptake based on log K_{ow} and PAH Ring Class	96
Table 2.17	Carrot Core PAH Concentrations at all Creosote Treatment Levels	100
Table 2.18	Carrot Peel PAH Concentrations at 50%, 15%, 1% and Control Treatment Levels	102
Table 2.19	Borradaile - Lettuce, Carrot and Barley at the Garden Site (Site G)	109
Table 2.20	Borradaile - Lettuce and Barley at the Drainage Channel Site (Site D)	111
Table 2.21	Borradaile - PAH Soil Concentrations Corresponding to Site G Lettuce, Carrot and Barley Vegetation	112
Table 2.22	Borradaile - PAH Soil Concentrations Corresponding to Site D Lettuce and Barley Vegetation	114
Table 2.23	Calculated Stem Concentration Factors (SCF) using Greenhouse and On-site Field Data	117
Table 2.24	Calculated Plant Concentration Factors using Greenhouse and On-site Field Data	118
Table 2.25	Level I Fugacity Based Model Calculations using Soil and Vegetation Concentrations from the 15% Creosote Contaminated Treatment	121
Table 3.1	Borrdaile - Lettuce, Carrot and Barley at the Garden Site (Site G)	140

Page

Table 3.2 Borradaile - Lettuce and Barley at the Drainage Channel Site (Site D) 142

Table 3.3 Borradaile - PAH Soil Concentrations Corresponding to Site G Lettuce, Carrot and Barley Vegetation 143

Table 3.4 Borrdaile - PAH Soil Concentrations Corresponding to Site D Lettuce and Barley Vegetation 145

Table 3.5 Calculated Contaminated Produce Concentrations - Base Estimate Case 147

Table 3.6 Measured Mean Contaminant Concentrations in Produce (Average of Barley and Lettuce Grown at the Borradaile Site) - Field Estimate Case 148

Table 3.7 Calculated Contaminant Concentrations for Direct Pathway Exposures of Receptors at the Borradaile Site - Base Estimate Case 150

Table 3.8 Calculated Contaminant Concentrations for Direct Exposure Pathways of Receptors at the Borradaile Site - Lower Estimate Case 150

Table 3.9 Measured Contaminant Concentrations for Direct Exposure Pathways of Receptors at the Borradaile Site - Field Estimate Case 151

Table 3.10 Base Estimate Case: Field Estimate Case Ratio 151

Table 3.11 Chronic Dose Estimates of Naphthalene for Adult Receptor 154

Table 3.12 Chronic Dose Estimates of Phenanthrene for Adult Receptor 155

Table 3.13 Chronic Dose Estimates of Chrysene for Adult Receptor 156

Table 3.14 Chronic Dose Estimates of Benzo(a)pyrene for Adult Receptor 157

Page

Table 3.15 Percent Exposure Contribution to the Chronic Dose of each PAH for the Adult Receptor - Base/Lower Estimate Case 158

Table 3.16 Percent Exposure Contribution to the Chronic Dose of each PAH for the Adult Receptor - Field Estimate Case 158

Table 3.17 Health Risk Summary for Maximal Lifetime Exposure of Naphthalene at the Borradaile Site 163

Table 3.18 Health Risk Summary for Maximal Lifetime Exposure of Phenanthrene at the Borradaile Site 164

Table 3.19 Health Risk Summary for Maximal Lifetime Exposure of Chrysene at the Borradaile Site 165

Table 3.20 Health Risk Summary for Maximal Lifetime Exposure of Benzo(a)pyrene at the Borradaile Site 166

Table 3.21 Borradaile PAH Concentrations of Selected Native Weeds and their Correspondingt Soil Concentrations 169

Table 3.22 Oil and Grease Content of the Borradaile Weed Soils 171

Table 3.23 Chronic Dose Estimates using Native Weeds from the Borradaile Site for the Adult Receptor 172

Table 3.24 Comparison of Actual to Estimated Data in the Plant Uptake Models 174

List of Figures

		Page
Figure 1.1	Generic Plant Model	8
Figure 2.1	Schematic Diagram of Each Experimental Growth Box in the Creosote Contaminated Greenhouse Experiment	41
Figure 2.2	Greenhouse Experiment Set-up	42
Figure 2.3	Map of the Borradaile Site	44
Figure 2.4	Pit #6 and Drainage Channel	45
Figure 2.5	Garden Site	46
Figure 2.6	XAD resin tube	54
Figure 2.7	Initial and Final Soil PAH Concentrations Detected in Each Treatment Level	68
Figure 2.8	Initial and Final Soil Concentrations for Each of the PAH Ring Classes for the Control Level	69
Figure 2.9	Initial and Final Soil Concentrations for Each of the PAH Ring Classes for the 1% Creosote Level	70
Figure 2.10	Initial and Final Soil Concentrations for Each of the PAH Ring Classes for the 15% Creosote Level	71
Figure 2.11	Initial and Final Soil Concentrations for Each of the PAH Ring Classes for the 50% Creosote Level	72
Figure 2.12	Initial and Final Soil Concentrations for Each of the PAH Ring Classes for the 100% Creosote Level	73

Page

Figure 2.13 PAH Air Concentrations in the Greenhouse from January - May 1993 75

Figure 2.14 PAH Air Concentrations in the Greenhouse from Week 5 to 14 76

Figure 2.15 Photograph of Carrot Yields 84

Figure 2.16 Barley: Percent Creosote Levels versus Experimental Treatments 92

Figure 2.17 Barley Vegetation "Normalized"-ratio of barley PAH concentration divided by the corresponding soil PAH concentration 93

Figure 2.18 Lettuce: Percent Creosote Levels versus Experimental Treatments 94

Figure 2.19 Distribution of PAHs by Ring Number for the Carrot Peel and Core at each Creosote Level (Control - 15%) 97

Figure 2.20 Distribution of PAHs by Ring Number for the Carrot Peel and Core at each Creosote Level (15% - 50%) 98

Figure 2.21 Total PAH Concentrations Detected in the Carrot Peels and Cores 105

Figure 2.22 Vegetative Uptake from Control - 15% Creosote Levels under the Worst Case Scenario for each type of Vegetation Investigated 106

Figure 2.23 Distribution of PAHs by Ring Number for the Control (C), Garden (G) and Drainage Site (D) Grown Lettuce and Soil 115

Figure 2.24 Distribution of PAHs by Ring Number for the Garden (G) and Drainage Site (D) Grown Barley and Soil 116

An Evaluation of Polycyclic Aromatic Hydrocarbon Exposure from Vegetation Grown in Contaminated Soil

1.0 Introduction

1.1 Background and Problem Statement

The Help End Landfill Pollution (HELP) Project of Alberta Environment has identified several contaminated sites in Alberta that are no longer owned by the parties responsible for the contamination. Two of those contaminated sites have been selected for the purpose of this study. These sites include a former petroleum processing facility and a former wood preserving site. In both cases the soil contamination of the sites are of complex organic mixtures that contain levels of polycyclic aromatic hydrocarbons (PAHs).

A primary concern with these contaminated sites is whether the residual contaminations pose any undue risk to human health. Because of this concern, a series of preliminary health risk assessments were performed at several of these contaminated sites. One of these, a former petroleum processing facility at Borradaile was evaluated for potential human health risk (Concord, 1991). In this assessment, very limited data was compiled to characterize the extent of contamination at the site. Consequently, to approach this problem many conservative assumptions and models had to be used to develop contaminant exposure and risk estimates. One set of assumptions sugggested that a maximally exposed individual living at the site would be exposed to benzo(a)pyrene, a PAH regarded as a probable human carcinogen, at levels thirteen times greater than that of a typical non-smoker and four times those experienced by a typical smoker. Furthermore, the risk assessment suggested that 88% of the benzo(a)pyrene exposure would arise from

ingestion of local products with 70% of this exposure attributed to produce grown in a garden, on-site.

The estimated risks for the most pessimistic set of assumptions (later referred to as the base estimate case) were higher than would normally be regarded as acceptable. Likewise the basis for the calculations was very hypothetical in view of the limited site characterization data. Consequently, there was substantial scope for field verification and experimental evaluation of likely exposures to PAHs arising from vegetation grown in PAH contaminated soil. The field data will allow for the re-evaluation and validation of the original human health risk assessment with respect to some of the assumptions used regarding polycyclic aromatic hydrocarbons (PAHs) exposure from soil and vegetation at this site.

1.2 Objectives

- Perform greenhouse and on-site plant growth experiments using PAH contaminated soils under partially controlled conditions to evaluate the pathways for PAH uptake by selected species of plants and evaluate the utility of an equilibrium Level I fugacity model.

- Evaluate the level of PAH contamination in soil and vegetation at the Borradaile site to assess the validity of the upper bound base case risk estimates.

1.3 Overall Approach

To sufficiently deal with the stated objectives, the overall approach to this study has been listed below:

- Analytical methods development;
- Field data collection on soils and native vegetation;
- Field growth experiments with PAH contaminated soils from the site;
- Greenhouse growth experiments with contaminated creosote soils with high levels of PAH exposure; and
- Evaluation of risk estimates using field data with respect to the original risk assessment.

The literature review follows to develop concepts for experimental approach.

1.4 Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons consist of two or more fused benzene rings in linear, angular, or cluster arrangements consisting only of carbon and hydrogen. The ring patterns and relative structural stabilities are indicated in Table 1.1 (Blumer, 1976). The structure and physical -chemical properties of the PAHs of concern in this study are listed in Table 1.2. The PAHs described are those listed in the U.S. Environmental Protection Agency's Priority Pollutant List and by the European Commission.

Table 1.1 PAH Ring Arrangement and Relative Stability (Blumer, 1976)

Ring arrangement	Linear	Cluster	Angular
Description	all rings in line	at least one ring surrounded on three sides	rings in step
Stability	least	intermediate	most
Example	anthracene	benzo(a)pyrene	phenanthrene

Sources of PAHs to the environment are both natural and anthropogenic. PAHs are ubiquitous constituents of crops, plants and algae in the natural and pristine areas. The highest reported natural background levels in vegetation have been for general broad leaf plants (22 to 88 parts per billion or ppb) (Sims and Overcash, 1983). Subsurface tap root vegetables (*i.e.* carrots, onions and beets) have exhibited the lowest concentrations (0.01 to 6.0 ppb). The distribution of PAHs among various vegetation is approximately: tree leaves (22 to 88 ppb) > cereals (48 to 66 ppb) > leafy vegetables (0.05 to 50 ppb) > subsurface vegetables (0.01 to 6.0 ppb) > fruits (0.02 to 0.04 ppb) (Sims and Overcash, 1983). Sources of anthropogenic PAHs originate from high temperature industrial processes (*e.g.* petroleum refining, wood preservation, manufactured gas plants and coke production) and are often associated with soil at former industrial sites. Because of the increase in fossil fuel consumption and industry's mismanagement of wastes over the past century, the environmental abundance of PAHs has increased (Jones, 1991).

Creosote is a complex chemical mixture that has been widely used as a wood preservative. It contains many constituents that have been reported to be mutagenic, teratogenic, and fetotoxic. It is composed of approximately 85% PAHs; 12% phenolic compounds; and 3% N-, S-, and O- heterocyclic compounds (Ekambaram, 1986 and Enzminger, 1987). PAHs include a group of organic priority pollutants of environmental and public health concern because of the following potential characteristics: chronic

Table 1.2 Structures and Physical-Chemical Properties of PAHs (cited from Sims and Overcash, 1983)

PAH	Molecular Weight	Structure (no. of rings)	Melting Point (°C)	Boiling Point (°C)	Aqueous solubility (mg/L)	log Kp	Vapor pressure (torr @ 20°C)
naphthalene	128	2	80	218	30	3.37	4.92×10^{-2}
acenaphthene	154	3	96	279	3.47	4.33	2.0×10^{-2}
acenaphthylene	152	3	92	265	3.93	4.07	2.9×10^{-2}
anthracene	178	3	216	340	0.07	4.45	1.96×10^{-4}
phenanthrene	178	3	101	340	1.29	4.46	6.80×10^{-4}
fluorene	166	3	116	293	1.98	4.18	1.3×10^{-2}
fluoranthene	202	4	111		0.26	5.33	6.0×10^{-6}
benz(a)anthracene	228	4	158	400	0.014	5.61	5.0×10^{-9}
chrysene	228	4	255		0.002	5.61	6.3×10^{-7}
pyrene	202	4	149	360	0.14	5.32	6.85×10^{-7}
benzo(a)pyrene	252	5	179	496	0.0038	6.04	5.0×10^{-7}
benzo(b)fluoranthene	252	5	167		0.0012	6.57	5.0×10^{-7}
benzo(k)fluoranthene	252	5	217	480	0.00055	6.84	5.0×10^{-7}
dibenz(a,h)anthracene	278	5	262		0.0005	5.97	1.0×10^{-10}
benzo(ghi)perylene	276	6	222		0.00026	7.23	1.0×10^{-10}
indeno(1,2,3-cd)-pyrene	276	6	163		0.062	7.66	1.0×10^{-10}

health effects; microbial recalcitrance; high bioaccumulation potential; and chemical persistence. The chemical persistence is due to low aqueous solubility, low vapor pressure and high log octanol-water partiion coefficient (log K_{ow})for the larger molecular weight PAHs (Table 1.2). Bos *et al.* (1983) determined that the mutagenicity of creosote was probably due to the presence of mutagenic PAHs.

One of the major problems in the health risk assessment of PAH contaminated soils involves the vegetative PAH uptake in a soil/plant system. The exposure of receptors (*e.g.* human),ingesting vegetative produce grown at a contaminated site must be considered as part of the dose estimate. Therefore verifying the routes of uptake, *via* air or soil into a plant is imperative. In these cases it is necessary to identify and quantify the predominant exposure routes of uptake into a plant. Estimates of vegetative uptake of PAHs can be made on the basis of the physical and chemical properties of the contaminants and soil contaminant matrix and relationships reported in published literature. However, "actual field data" can be used to verify these estimates in risk assessments.

In the current literature, three main exposure pathways for PAH uptake into a plant system have been accepted (Ryan *et al.*, 1989 and Curtis *et al.*, 1988). These are:

i) uptake of PAHs through root tissues by translocation (Topp *et al.*, 1986, Briggs *et al.* 1982 and 1983, and Trapp *et al.* 1990),

ii) adsorption of PAHs to the root surfaces by soil contamination,

iii) foliar uptake of PAHs which have been volatilized from the soil or deposited from the atmosphere, (Wild and Jones 1990, 1991c, 1992d, Kerler *et al.*, 1984) and

The amount of PAHs found in a plant is determined by the effectiveness of the various pathways for PAH uptake. To comprehend the possible uptake of PAHs, it is necessary to understand the structure and water and nutrient flow mechanisms of a typical plant.

1.5 Plant Model Structure

The two possible structural entry routes of contaminants into a plant system are through the root system and/or the shoot system which is comprised of foliage, fruit and stem. The structure, nutrient movement and chemical uptake of the plant were based on a generic plant model shown in Figure 1.1.

The structure of a plant can be characterized with respect to its growth, structure and function. To understand root functions, the characterization of individual cell types of primary root tissues is important. Differentiation of primary root tissues- epidermis, primary cortex and central cylinder (stele), starts as early as in the root meristem (Salisbury and Frank, 1992). Meristem cells, from which these root tissue types differentiate, become morphologically distinct and the root pattern is formed (Salisbury and Frank, 1992).

During primary growth the root surface is covered by the epidermis (rhizodermis). It consists of one layer of cells which, by structural properties of their cytoplasm and cell walls, are specialized as an absorption tissue. In mature stages of the plant, the epidermis acts as a protective layer. An important property of epidermal cells is the formation of root hairs. The region of primary cortex is located under the epidermis. The cortex makes up a considerable part of the root volume. Its ratio to the central cylinder is greater in the root than in the stem. The cortex or outer tissue of the root contains the "apparent free space", occupying 10 to 20% of the root volume (Paterson *et al.*, 1990). The central cylinder

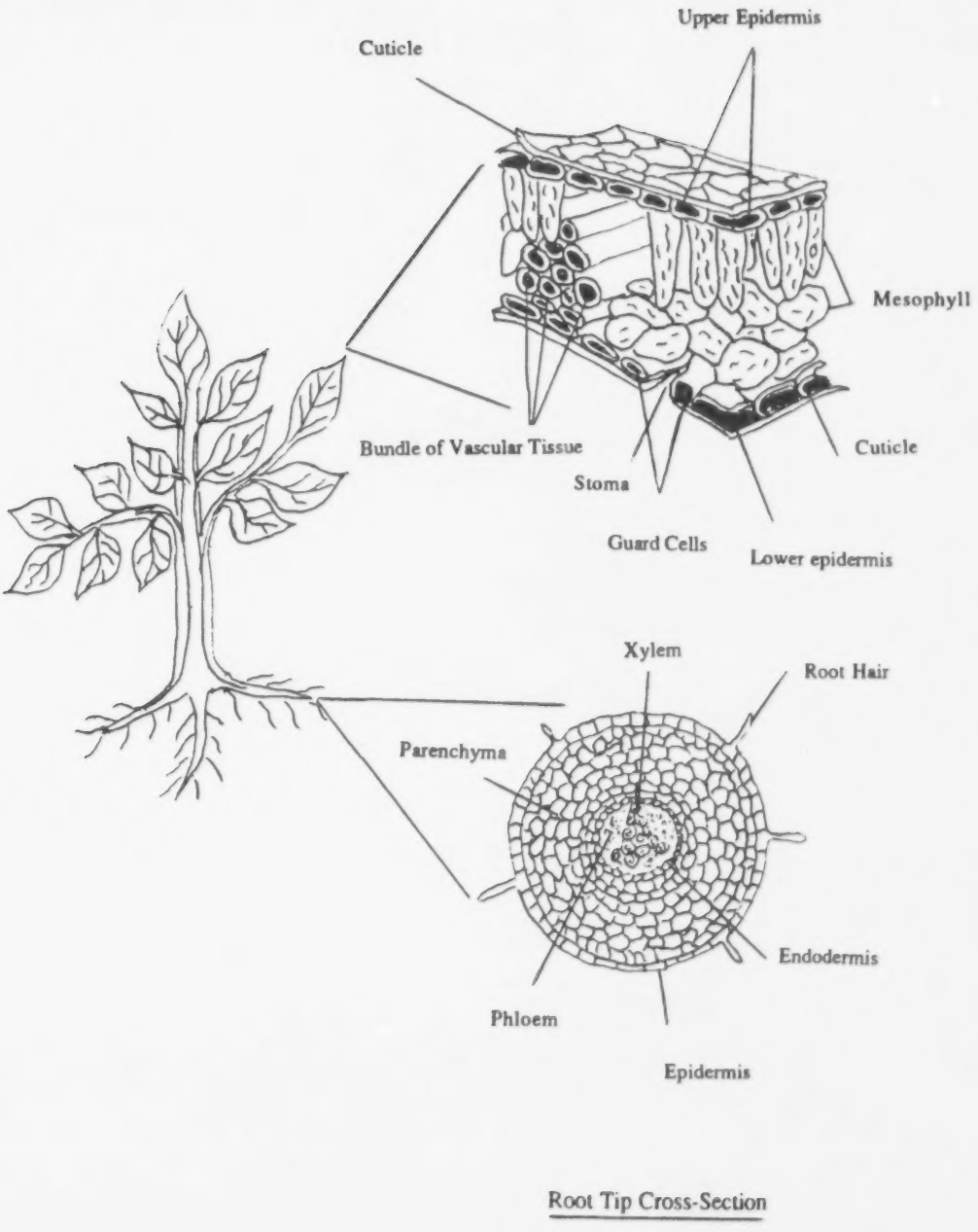

Figure 1.1 Generic Plant: adapted from Alberts *et al.*, 1983

(stele) can be imagined as a column in the centre of the root, formed by the pericycle and filled with primary vascular tissue. The structure of the stele corresponds to its function, transport of water and nutrients. Just outside of the stele is a layer of cells called the endodermis. The endodermal cells are important from the aspect of water movement since their radial and transverse cell walls include thickenings called Casparian strips that are impermeable to water (Schraer and Stoltze, 1990).

The primary vascular tissue within the stele are the primary xylem and the primary phloem. The main function of the xylem is translocation of water and solutes taken up by the roots and delivery to the synthesis sites in the plant leaves. The phloem transports the assimilates, substances photosynthesized (*e.g.* sucrose), from their synthesis sites to their utilization sites. The xylem tissue in the root center is continuous with the xylem tissue in the stem. It is also closely associated with phloem tissue as the diameter of the root increases during growth (Bidwell, 1974).

The apical meristem of the shoot divides and differentiates to become the primary tissues of the stem. The epidermis of the stem is one cell thick and provides protection from moisture loss. The epidermal cells secrete a layer of waxy substances, the cuticle. The cuticle of the stem is continuous with a layer of cuticle that covers the leaves.

The main function of the stem are:

i) to support structures of the shoot system,

ii) to transport substances between the root and leaves *via* the xylem and phloem transport systems,

iii) to also store substances synthesized in the leaves in the amyloplasts.

As in the primary root and stem, the leaf's outer surface, both top and bottom, is covered by the epidermis. The epidermal cells of leaves, like those of stems secrete a waxy, water proof cuticle. Most of the cuticle is composed of a heterogeneous mixture of components collectively called cutin, while the remainder consists of overlaying waxes and of pectin polysaccharides attached to the cell wall. Cutin is a heterogeneous insoluble polymer composed of crosslinked hydroxy-fatty acids (Riederer and Schonherr, 1984).

Between the epidermal layers of the leaf are two layers of mesophyll, the photosynthetic tissues that make up the bulk of the living matter in the leaf. The leaf also has vascular tissue, running through the mesophyll. The vascular tissue brings water to the leaves from the roots, and carries away the synthesized products of photosynthesis.

The cuticle is not continuous over the surface of the leaf but is interrupted at intervals by stomata. Each stoma is a pore between a pair of lip-like guard cells. The size of the pore can be controlled by the guard cells. The leaf's waterproof cuticle helps to reduce evaporation, but since it is relatively impermeable to gases, it also prevents the leaf from obtaining carbon dioxide for photosynthesis through much of its surface. When the stoma is open, carbon dioxide can enter the plant, but also more water vapor can escape (transpiration) into the atmosphere. Evaporation, regulated by the stomata creates the transpiration driving force that controls the xylem flow from the roots. Closing the stoma reduces the exchange of these gases between the interior of the leaf and the atmosphere (Schraer and Stoltze, 1990).

Environmental factors that affect transpiration include the availability of water in the soil, the intensity of sunlight, the relative humidity, temperature, and wind speed of the air.

1.6 Water and Nutrient Movement

The transport of water and nutrients from the soil to the leaves is a polarized flow proceeding in three steps:

i) uptake by the root cells;

ii) radial transport through root tissues into the xylem; and

iii) longitudinal transport through the xylem into the shoots.

The first stage of water and ion uptake by roots is their entrance into the apparent free space (AFS) of the root system. AFS involves intercellular spaces, cell wall and the space between cell walls and the cytoplasm. Ion uptake in the AFS is associated with exchanges at labile binding sites on AFS surfaces, in the Donnan free space (DFS). The prevalence of negatively charged sites in DFS is due to cation exchange capacity. In water movement the following forces have frequently been distinguished (Kolek and Kozinka, 1992):

i) forces causing passive movement by diffusion or volume flow;

- *diffusion* . This process involves water movement driven by the difference in water potential on the two sides of the membrane. The water potential depends mainly on: the osmotic potential, due to the presence of solutes and the hydrostatic pressure. The most common examples of diffusion movement of water in a plant are evaporation and osmosis.

• *volume flow (mass).* This process occurs when differences in pressure potential or hydrostatic pressure are the driving force. An example of volume flow is water movement induced by gravity.

ii) active transport causing active movement depending on the consumption of metabolic energy. The active component is not water flow but accumulation of osmotically active substances.

Ions dissolved in water (solutes) will follow the movement of water in the root by diffusion, DFS, and osmotic pressure gradients. These types of transport are non-metabolic, *i.e.* independent of energy supplied by metabolism.

Active transport is also involved in the movement of substances. Kedem (1961) characterized active transport as a coupling of two flows. The primary active transport process is coupled with release of metabolic energy from ATP hydrolysis. The secondary active transport of metabolites, *e.g.* saccharides and amino acids, is coupled with the proton pump (H^+) across the membrane.

The endodermis and stele exert a resistance to the flow of water which is approximately 100,000 times higher than the resistance of conducting elements of the xylem to longitudinal flow (Weatherley, 1982). Radial movement of water to the tissues may occur by three pathways:

i) movement from the vacuole of one cell to the vacuole of another cell;

ii) movement in the symplast; and

iii) movement via the cell walls - apoplast (Weatherley, 1982).

Once past this barrier, the xylem provides the passage of water and nutrients to the rest of the plant - stem and leaves.

Since there is no living matter in the conducting cells of xylem, xylem conduction must depend on passive rather than active transport. Two transport processes that have been confirmed are capillary action and root pressure. Capillary action involves the cohesive and adhesive nature of water causing it to move into small spaces lined with polar molecules, even against the pull of gravity. Thus water slowly moves up the walls of the vessels. The process of transpiration or the evaporation of water from leaves, can create a cohesive or pulling force so water and nutrients can travel up the longitudinal vessel. The rate of transpiration is regulated by the opening and closing of the stomates of the leaves which control the rate of water loss by evaporation.

The phloem transports the assimilates at a high rate, compared to that of the xylem. The main substance transported by the phloem is sucrose, in concentrations up to 25%. The movement of the assimilates, such as sucrose, from the leaf to the phloem conducting cells is by active transport. Phloem also carries nucleotides, hormones, and various other organic compounds.

An interconnection of pathways and flows exist for the xylem and phloem. In principle the interconnection is possible in two ways, through the cytoplasmic continuum and through the extra-protoplasmic compartment (Giaquinta, 1983). With the counter current movement of water and solutes in the xylem and phloem between the source-leaf and the sink- roots, the presumed main solute exchange will take place at both poles of the conducting pathways, in leaves and root tips.

1.7 Chemical Uptake in the Plant

Studies to date have shown chemical uptake and distribution within the plant is affected by contaminant soil concentrations, contaminant solubility, vapor pressure, molecular size, support media anchoring the plants and the plant species. Briggs *et al* (1982) and Topp *et al.* (1986) have shown that uptake of many compounds into plant roots from soil aqueous solution is inversely proportional to water solubility, but transfer to shoots is more efficient for chemicals of intermediate solubility. With respect to PAHs, plants have greater concentrations on the leaf surface compared to the internal tissues because of the PAHs high degree of hydrophobicity, they bind to the cuticle (Edwards, 1983). Narrow leafed plants contain less PAHs than broad leafed plants because of the larger surface area for entrapment of the volatile PAHs (Edwards, 1983). Uptake and translocation of PAHs *via* the plant root system has been reported by some research groups while disputed by others.

Highly hydrophobic PAHs such as benzo(a)pyrene will tend to bind to the root surface (Wild and Jones, 1992c). Uptake by the roots has shown selective translocation of PAHs, with linear configured PAHs (anthracene and benz(a)anthracene) being taken up more easily than nonlinear PAHs (phenanthrene) (Weber *et al.*, 1984). Experiments reporting uptake of PAHs in carrots, reveal carrots peels to retain the majority of the PAH burden, with a decreasing load moving to the core (Wild and Jones, 1991b). High concentrations of PCB have been found associated with the outer cell walls in carrots. Carrots have a lipid rich peel and perhaps represent the "worst case" for root uptake from contaminated soils (Wild and Jones, 1992c).

Adsorption of PAHs onto the root surfaces may be an important process causing

PAH incorporation into root tissues. Once adsorbed, the low solubility and higher molecular weight PAHs are not expected to be translocated (Briggs *et al.*,1982 and Wild and Jones, 1990). Uptake of hydrophobic organic compounds is lower in soils with high organic matter content due to the greater potential for adsorption of the hydrophobic compounds to the soil organic matter (Ryan *et al.*, 1988). Therefore, the amount and nature of the soil organic matter is also a determining factor for root uptake of PAHs.

Studies have suggested foliage uptake of organic chemicals to dominate over root translocation (Bacci and Gaggi, 1986). Routes of entry of chemicals to foliage include deposition in association with dust or atmospheric particulate matter and uptake from surrounding vapors by adsorption to the shoots. Hydrophobic chemical (PAH) uptake *via* foliage tends to be more probable than root uptake because:

i) the total leaf surface exposure area may exceed the soil surface exposure area by a factor of 20 (*e.g.* lettuce);

ii) the low aqueous solubility and strong sorption of hydrophobic (lipophilic) compounds in soil tends to retard the mobility of these chemicals; and

iii) plant surfaces above-ground have greater permeability for hydrophobic chemicals than roots.

Uptake of organic chemicals by the leaves may proceed by two independent pathways:

i) organic chemicals adsorbed to particulates must penetrate by dissolution into the cuticle before they reach the internal tissues (Kerler and Schonherr,

1988b) while,

ii) volatiles can also enter through the open stomata (Sabljic *et al.*, 1990).

All non-volatile organics reaching the above-ground plant surface must penetrate through a cell wall covered by a cuticle, so the process of penetration may be different than sorption to a root which does not possess this type of protective cover (Topp *et al.*, 1986). The cuticle as described earlier is composed primarily of wax and could therefore bind and store lipophilic compounds such as PAHs. The tendency to be retained by the cuticle is strongly dependent on the chemical's octanol-water partition coefficient (K_{ow}). Therefore, for volatile compounds, diffusion in the vapor phase and subsequent uptake by the root and/or shoot may be an important route of chemical entry into the plants. For semi-volatile compounds with high log K_{ow} (>4.5) and low vapor pressure, translocation from the root system could be minimal. However, semi-volatiles may bind strongly to aerosols, which can then be deposited on plant foliage. It is suggested, that once the organic compound binds to the cuticle, diffusion through aqueous routes in the cuticle to the apoplast can occur *via* carbohydrate fibres of the epidermis. The process of diffusion may occur in both the aqueous and lipid phases of the cuticle (Paterson *et al.*, 1990). Some PAH compounds may be metabolized once inside the plant leaf tissues and the by-products translocated throughout the plant (Edwards, 1986).

1.8 Plant Uptake Correlations

Many correlations have been developed to present the relationship of contaminant concentration within root, stem and leaves to those in the soil and air. Briggs *et al.*, (1982, 1983), Ryan *et al.*, (1988), Topp *et al.*, (1986), Bacci *et al.*, (1987), Kerler and Schonherr (1988), Trapp *et al.*, (1990) and Travis and Arms (1988) have all developed correlations

dealing with organic chemical uptake into plants. General observations dictate hydrophilic chemicals are more readily adsorbed into the root system and translocated to the leaf. While hydrophobic chemicals tend to sorb more strongly to the soil, they are generally less available to the plant from the soil.

Recent work by Topp *et al.*, (1986) and Bacci *et al.*, (1987) have investigated chemical exposure to plants via soil-air-leaf route. Bacci *et al.*, (1990a, 1990b) have shown the dependence of plant bioconcentration factors (BCF) to air-water and octanol-water partition coefficients for selected chemicals.

Shone and Wood (1974) proposed that uptake of a chemical can be described by a root concentration factor (RCF), defined as:

$$RCF = \frac{\text{concentration in root (}\mu\text{g of contaminant/g of fresh weight)}}{\text{concentration in external soil aqueous solution (}\mu\text{g contaminant/mL aqueous solution)}}$$

This RCF can only be used in a low contamination soil medium where the concentration in the roots will be linearly related to the concentration in the soil medium. Assuming that RCF can be explained by partitioning of a chemical in the roots and soil and a small uptake that is constant for all chemicals (0.82), Briggs *et al.* (1982) described partitioning as:

$$\log (RCF - 0.82) = (0.77 \log K_{ow}) - 1.52 \qquad (1)$$

showing a positive correlation between the RCF and the octanol-water partition coefficient (K_{ow}) as might be expected. RCF increased with increasing K_{ow}, meaning that more lipophilic chemical compounds exhibit a stronger affinity to the root.

The efficiency of the translocation of a chemical from the roots to the shoots has been described by the transpiration stream concentration factor (TSCF). This factor is defined as:

$$TSCF = \frac{\text{concentration in the transpiration stream (}\mu\text{g of contaminant/mL water transpired))}}{\text{concentration in the external soil aqueous solution (}\mu\text{g of contaminant/mL aqueous solution)}}$$

and, Briggs *et al.* (1982) reported the nonlinear relationship:

$$TSCF = 0.784 \exp - [(\log K_{ow} - 1.78)^2 / 2.44] \qquad (2)$$

They evaluated plant uptake and found TSCF was less than 1.0 for all chemicals, suggesting only passive transport in the shoot by the transpiration stream. The chemicals tested for uptake were O-methylcarbamoyloximes derivatives and substituted phenylureas by barley from nutrient solutions. Their relationships indicate that translocation to foliage was most efficient for chemicals with log K_{ow} near 1.8. At log K_{ow} values exceeding 1.8, translocation of chemicals is limited by the rate of transport of the lipophilic compounds up through the shoots. At log K_{ow} values less than 1.8, translocation is limited by the lipid membrane in the root.

Briggs proposed an analogous stem concentration factor (SCF) to the RCF where SCF is defined as:

$$SCF = \frac{\text{concentration in stem (}\mu\text{g of contaminant/ g fresh weight)}}{\text{concentration in external solution (}\mu\text{g of contaminant/ mL of solution)}}$$

They showed macerated barley stem sorption of organic compounds was also related to the K_{ow}.

$$\log SCF_{(macerated\ stems)} = 0.95 \log K_{ow} - 2.05 \quad (3)$$

Briggs *et al.* (1983) assumed that the concentration of the aqueous phase in the stem was similar to the roots in the uptake process. Therefore the partitioning between the stem and the xylem sap or transpiration stream can be predicted:

$$\log (K_{stem/xylem\ sap} - 0.82) = 0.95 \log K_{ow} - 2.05 \quad (4)$$

The SCF was then established as a product of this stem/xylem sap partition coefficient multiplied by the TSCF, the fraction of the external solution present in the xylem sap:

$$SCF = K_{stem/xylem\ sap} \times TSCF \quad (5)$$

resulting in:

$$SCF = [\ 10^{(0.951 \log K_{ow} - 2.05)} + 0.82]\ 0.784 \exp - [\ (\log K_{ow} - 1.78)^2/2.44] \quad (6)$$

The above relationships are only be applicable under equilibrium conditions.

Experiments using radiolabelled organic chemicals for tracing movement (Topp *et al.*, 1986), showed a negative correlation of root uptake from the soil to the soil adsorption coefficients (K_{oc}) based on the soil organic carbon content. This suggests that only chemicals not adsorbed to soil organic carbon are readily accessible for plant uptake. However, uptake from soil aqueous solution also correlated positively to octanol-water partition coefficients which are positively correlated with K_{oc}. There is also a difficulty in predicting uptake because the partition coefficients rely on equilibrium which may be reached slowly or not at all in these short term experiments. Their resulting correlations are:

$$\log RCF\ (soil) = 2.196 - 0.622\ \log K_{oc} \quad (7)$$

and

$$\log RCF\ (water) = -0.959 + 0.630\ \log K_{ow} \quad (8)$$

Topp *et al.* (1986) also correlated barley foliar uptake (FU) with volatilization from soil (VOL) with a short term laboratory experiment. The proposed relationship was:

$$FU = 46.11 - 28.98\ \log VOL \quad (9)$$

where:

FU = foliar uptake in percentage of total ^{14}C uptake

VOL = organic ^{14}C trapped from the air + ^{14}C sublimated on the glass walls as percentage of ^{14}C initially applied

The equation describes the relationship between uptake of chemicals from soil via air and volatilization from soil.

Topp *et al* (1986) did experiments comparing uptake with molecular weight of several chemicals (*e.g.* benzene derivatives - pentachlorophenol) and found molecular weight was a more important factor predicting root uptake than was K_{ow}. for the chemicals they tested

$$\log CF = 5.943 - 2.385\ \log M \quad (10)$$

where:

$$CF = \frac{\text{concentration in plants (based on fresh weight)}}{\text{concentration in the soil (based on dry weight)}}$$

M = molecular weight.

Schonherr and Reiderer (1989) and Kerler and Schonherr (1988b) showed that the transport of organics across the cuticle is deterimined by both the solubility and mobility within the cuticle. The solubility in the cuticle is characterized by the cuticle-water partition coefficient (K_{cw}). Kerler and Schonherr (1988a) showed the cuticle-water partition coefficient (K_{cw}) and the octanol-water partition coefficient (K_{ow}) were similar in magnitude. Plants with thick cuticles as fruits and tomatoes, allowed for very little mobility of organic compounds with log K_{ow} greater than 5 (Riederer and Schonherr, 1984).

Kerler and Schonherr developed a correlation between permeability coefficient of the cuticle P(CM) for a number of chemicals with log K_{ow} values between 1.92 and 7.86, K_{cw} and molar volume of the chemical:

$$\log P(CM) = \frac{238 \log K_{cw}}{MV} - 12.48 \qquad (11)$$

where:

P(CM) = permeability coefficient of the cuticles

K_{cw} = cuticle - water partition coefficient

MV = molar volume (cm^3/mol)

Sabljic *et al.* (1990) used molecular connectivity indexes to show molecular size is directly proportional to the cuticle-water partition coefficients. Molecular connectivity indices describe and quantify the size, the shape, the degree of branching and the cyclicity of molecules. Using the molecular connectivity model they were able to predict K_{cw} with accuracy and faster than the use of empirical models based on water solubilities. With the accuracy of predicting K_{cw}, it will make it possible to estimate the rate limiting step in chemical transport across the cuticle and determine the accumulation potential of air pollutants.

Assessing the degree of human exposure to food ingestion depends on the prediction of accumulation in the food chain. Travis and Arms (1988) have indicated octanol-water partition coefficients to be a useful in predicting food chain accumulation. Biotransfer factors for organic chemicals in beef (B_b) and milk were presented as being directly proportional to K_{ow}:

$$\log B_b = -7.6 + \log K_{ow} \qquad (12)$$

where:

B_b = concentration in beef (mg/kg) / daily intake of organic (mg/d)

K_{ow} = octanol - water partition coefficient

They reported the bioconcentration factor (BCF) for vegetation (B_v) to be inversely proportional to approximately the square root of K_{ow}.

$$\log B_v = 1.588 - 0.578 \log K_{ow} \qquad (13)$$

where:

B_v = concentration in vegetation (mg/kg) / daily intake of organic (mg/d)

K_{ow} = octanol - water partition coefficient

This supports the theory that translocation depends on a chemical's solubility which is inversely proportional to K_{ow}.

Bacci *et al* (1990a, and 1990b) have taken predicted leaf-air BCF ($BCF_{leaf/air}$) from their studies to develop a correlation with air-water and octanol-water partition coefficients. An equation is shown below:

$$BCF_{leaf/air} = 0.022\ K_{ow} / K_{aw} \qquad (14)$$

where:

$$BCF_{leaf/air} = \frac{\text{concentration of contaminant in the leaf (mg/kg)}}{\text{concentration in the air (mg/m}^3\text{)}}$$

K_{ow} = octanol - water partition coefficient

K_{aw} = air - water partition coefficient

which can be transformed to ($K_{ow} / K_{aw} = K_{oa}$),

$$BCF = L \bullet K_{oa} \qquad (15)$$

where:

K_{oa} = octanol - air partition coefficient

L = lipid factor (vol/vol) in the plant leaf

Reisch (1989) developed an equation to predict leaf-air BCF based on K_{ow} and Henry's law constant, H, in an experiment using spruce needles.

$$BCF_{leaf/air} = 1696\ (K_{oa})^{0.42} \qquad (16)$$

(rearranged to compare to Bacci *et al* (1990) equation above)

Predictions (Bacci *et al.*, 1990b) of BCF based on these two equations (15 and 16) are only similar if K_{oa} is of the order of magnitude of 10^8. Otherwise discrepancies arise suggesting the need for more refinements to these equations to apply over a wider range. However, it can be stated that the main factors controlling leaf-air equilibrium for non-polar and non-reactive chemicals are its water solubility, vapor pressure and the lipid content of the leaf.

Paterson *et al,* (1991a) have also suggested a correlation for the leaf-air BCF as a function of a chemical's water-air and octanol-air partition coefficients and the leaf properties of air, water and octanol equivalent volume fractions. The leaf - air volumetric bioconcentration factor is expressed as a function of the chemical's water - air and octanol - air partition coefficients and three constants characteristic of the leaf properties. Values of the constants have been estimated for azalea leaves.

$$BCF_v = y_a + y_w/K_{aw} + y_oK_{ow}/K_{aw} = y_a + y_w/K_{wa} + y_oK_{oa} \qquad (17)$$

where:

y_a = volume fraction of air

y_w = volume fraction of water

y_o = volume fraction of octanol

K_{wa} = water - air partition coefficient

K_{oa} = octanol - air partition coefficient

Paterson *et al.*(1991a) suggested that this equation gives a satisfactory representation of air - leaf equilibrium for conservative hydrophobic organic chemicals. Experiments were done using azalea leaves, but clearly more data using different leaves and chemicals is required for further validation. The literature suggests, that K_{oa} is the key partitioning descriptor for hydrophobic chemicals. Caution must be taken when testing this correlation against field data because this vapor - transfer correlation does not include aerosol or particulate associated chemical deposition.

1.9 Uptake Models

With the lack of comprehensive experimental data it is difficult to assess, quantitatively, the partitioning and transport processes of chemicals in the foliage-atmosphere system. Estimates derived from a mathematical model of this system may serve as first approximations. Mackay and Paterson (1981) proposed the "fugacity model" approach to calculate the relative amount of substance that will partition into major compartments of the environment.

More recently, Paterson and Mackay (1989, 1990 and 1991b) developed the fugacity model for a hypothetical plant. The first simple Level I model has the plant divided into three compartments: root, stem and leaves with defined volumes. The chemical concentration in the plant compartments are estimated from input air and/or soil concentrations. The equilibrium model uses fugacity capacities, or Z values, to describe the partitioning within the plant (see Appendix C). Z values were developed from modified correlations from work by Briggs *et al* (1982), Calamari (1987) and Kerler and Schonherr (1988a). Reiderer (1990) has used the fugacity based model to estimate partitioning and transport of organic chemicals in the foliage-atmosphere system. The simpler Level I and Level II models, although useful as a starting point, have the severe weakness that they are constrained by the assumption of inter-phase equilibrium (*i.e.* each compartment has equal fugacity). In reality this is rarely achieved and this assumption can be misleading. Mackay and Paterson (1991a) have also developed a dynamic Level III model that significantly differs from the previous fugacity models. The compartments are treated as assemblies of subcompartments where equilibrium is assumed to apply within each subcompartment, but not between compartments. Early evaluative fugacity models treated only diffusive-transfer processes such as volatilization and absorption, while Level III includes nondiffusive or "one-way" processes in which chemical is conveyed between media by association with

material that is undergoing intermedia transfer. The Level III model deals with processes such as: partitioning; all degrading reactions- hydrolysis, oxidation, photolysis and biolysis; advection; interphase transport- solute transfer processes and material transfer processes; and diffusive and nondiffusive transfer processes. This will be important for hydrophobic chemicals because time for their uptake may be long compared to the life of the plant.

Other models of this type have been developed by Calamari (1987) who has included a terrestrial biomass compartment in the fugacity based Level I model ; Boersma and co-workers developed a comprehensive compartmental model of a soybean plant where uptake, transport and accumulation of a chemical are described by a series of mass balance equations (Boersma *et al.*, 1988) and Trapp *et al* (1990) investigated the bioconcentration of organic contaminants into barley.

Recently Boersma, McFarlane and Lindstrom have developed a mathematical model called UTAB (Lindstrom *et al.*, 1991), based on principles of concentration of mass and xylem/phloem transport. The model adequately simulated experimental results tracing uptake of bromacil by a soybean plant (Boersma *et al.*, 1991).

1.10 Experimental Designs and their Uncertainties

Despite the growing bibliographic information that serves as the basis for studies of contaminant uptake into vegetation, several uncertainties remain. For instance, many studies have dealt with the plant uptake of PAHs from soil. The major emphasis of research has been devoted to the study of benzo(a)pyrene behavior, which does not necessarily correlate with the behavior of other PAHs (Sims and Overcash, 1983). The

emphasis on benzo(a)pyrene is likely based on its carcinogenic properties that make it relevant for health risk assessment.

Further problems arise because of the difficulties of obtaining reliable measurements of uptake. Tracer studies with ^{14}C radiolabelled chemicals are often ambiguous because the radioactivity measured in the plant is not necessarily associated with the unmetabolized parent compound. This concern is of great importance for PAHs that can be metabolized rapidly by the plant; some show half lives under 10 days (*e.g.* naphthalene) (Topp *et al.*, 1986).

In most cases with ^{14}C radiolabelled experiments data for long term experiments are needed because with short term experiments equilibrium in the solution-plant system has not been achieved. Although equilibrium is not reached in the time span of such short term experiments, rough estimates of root concentration factors are extrapolated. Under such circumstances, the correlations developed by researchers may not be useful for mechanistic models. For example, Brigg's RCF correlation may not reflect equilibrium conditions for more hydrophobic chemicals such as PAHs because of the short term experiments.

Experiments involving spiking the soil with cocktails of PAHs or other chemicals of environmental concern are also problematic. Soils mixed with such chemical cocktails do not necessarily mimic the behavior of chemicals found in a contaminated soil. In such cases, the chemicals do not have the time to equilibrate with the aqueous solution and organic matter and allow for the absorption/diffusion process to occur within the soil micropores, as would be the case with actual contaminated soil. Also, estimates of persistence of organic chemicals from controlled laboratory experiments with spiked solutions of ^{14}C labelled compounds may bear little resemblance to field observations when the contaminant enters the soil under realistic conditions.

Briggs (1982 and 1983), McFarlane (1985 and 1987) and other researchers have investigated translocation using excised barley in ^{14}C-labelled chemicals solutions. This set-up can only deal with passive transport and overlooks the much more complex mechanisms of chemical uptake into plants.

Wild and Jones (1990, 1991a, 1991b, 1991c, 1992a, 1992b, 1992c and 1992d) have presented a series of papers pertaining to plant uptake of PAHs in soils of "normal" PAH abundance. They have rightfully criticized experiments using excessive, unrealistic soil PAH concentrations for obtaining generalized relationships. With soil concentrations at part per billion (ppb) levels it is difficult to discern mobility of PAHs. These levels are so low that detectable PAHs may be artifacts of the analytical method used. Most of the work done by Wild and Jones have dealt specifically with PAHs in sludge amended soils in long-term experiments, where the high organic matter content of soil retards plant uptake of PAHs. Long-term experiments (years) do not focus only on plant uptake since crops are essentially transient, they are harvested and removed from the soil at regular intervals.

Most experimental studies discussed previously have not been designed to distinguish between the two principal pathways of uptake:

i) root uptake and subsequent translocation and

ii) foliar uptake of vapors from the surrounding air space.

Recent studies have stressed the importance of foliar uptake directly into the above ground portion of the plant compared to root uptake and translocation of volatile and semi-volatile compounds (Bacci *et al.*, 1990a, 1990b and Trapp *et al.*, 1990).

With this review of the literature it is evident that an investigation to establish which pathways are predominant in PAH uptake into plants must have an appropriate experimental design. This is because of

- the physical-chemical properties of PAHs;
- the properties of the soil/plant system;
- correlations are based on more hydophilic chemicals; and
- most experiments deal with short-term experiments using simulated contaminated soil created by chemical cocktails or ^{14}C-radiolabelled chemical solutions.

An awareness of the relation of contaminants with the plant uptake mechanisms will also aid in the refinement of risk assessment approaches for abandoned industrial sites with PAH residues.

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An Investigation of Vegetative Uptake of Polycyclic Aromatic Hydrocarbons

2.0 Introduction

The Alberta Environment HELP Project has undertaken the investigation and risk assessment of selected abandoned refinery and wood preserving sites in the province. The risk assessments performed to date indicate that some key assumptions regarding polycyclic aromatic hydrocarbon (PAH) uptake at these sites require validation. Of specific concern are those assumptions relating to PAH uptake by vegetation.

One of the major complexities in evaluating health risk associated with vegetative PAH uptake in a soil/plant system is to identify and quantify the important exposure routes. Inferences for PAHs can be drawn based on the physical and chemical properties of the contaminant and soil contaminant matrix; however, "actual field data" can verify assumptions made in risk assessments.

Studies to date have shown chemical uptake and distribution within plants is affected by PAH concentrations, solubility, vapor pressure, molecular size, support media anchoring the plants and plant species (Edwards, 1983 and Ryan *et al.*, 1988). Plants have been shown to have greater PAHs on surfaces compared to internal tissues and narrow leafed plants contain less PAH than broad leafed plants (Edwards, 1983) suggesting an important role for foliar uptake. Uptake and translocation of PAHs *via* the plant root system has been reported by some research groups while disputed by others because of the very low water solubility of higher molecular weight PAHs. However, if translocation does occur it will likely be a small part of the above-ground plant PAH load: the majority of

PAH associated with plants is likely to result from direct atmospheric deposition and soil splash onto the leaves and shoots.

Several uncertainties associated with PAH uptake in a soil/plant system remain because: (i) most studies use a limited number of PAH compounds, (this can be misleading because of the range of physio-chemical properties possessed by PAHs), (ii) studies spiking PAHs into soil. do not mimic the behavior of PAHs found in a real contaminated soil, (iii) use of radiolabelled studies does not distinguish if ^{14}C detected in the plant tissue is the parent compound or a breakdown product (Wild *et al.*, 1992).

To investigate the exposure pathways in PAH uptake in plants, an appropriate experimental design must be implemented. In this study, two types of growth experiments were conducted, a greenhouse and on-site growth experiment. The greenhouse growth experiment was set-up using highly contaminated creosote soil that produced high exposure levels of PAHs. Selected species of plants were grown in growth boxes at each given level of creosote (*e.g.*100%, 50%, 15% and 1%). Within each creosote level, three PAH exposure routes were investigated: air particulate deposition, vapor transport from soil to foliage and uptake by root translocation.

The on-site growth experiment was conducted at a former petroleum processing facility at Borradaile. This site had previously been evaluated for potential human health risk by Concord (1991). Because of limited data gathered from the site and with the estimated risk being unacceptable, there was sufficient lattitude to carry out verification and experimental evaluation of PAH exposure arising from vegetation grown on-site. The experimental design was similar to that of the greenhouse experiment, with the three exposure routes being investigated. Four locations on the site were selected for the growth experiment based on preliminary data from a report prepared by Pollard and Hrudey

(1992); the garden (site G), drainage channel (site D), the background (site B) and the control (site C) . The Borradaile on-site experiment allowed for the plants to be grown with local contaminated soil under local weather and growth conditions.

2.1 Methods and Materials

2.1.1 Creosote Contaminated Soil Greenhouse Experiment

The creosote for the greenhouse experiment was obtained from a decommissioned wood preservative plant which operated from 1924 to 1987. The plant produced creosote treated products such as railway ties, foundation pilings, utility poles and fence posts at a production level of 60,000 to 90,000 m^3 of wood products per annum . The types of wastes produced from this facility were derived from creosote, pentachlorophenol, chromated copper arsenate and ammoniacal copper arsenate (PCP, CCA, and ACA). The creosote collected from the site was from an old drainage ditch which was being excavated and placed in a lined rectangular pit for reclamation. Soil samples from this pit were previously analyzed for PAHs before 2.0 m^3 of creosote contaminated soil was collected. The soil composition was 52% sand, 23% silt and 25% clay.

2.1.1.1 Experimental Design

The creosote was diluted with clean topsoil to investigate the relative levels of PAH uptake into different plant species in relation to the range of contamination. To prevent leaching from washing PAHs through the bottom of the boxes in which plants were grown, a polypropylene liner was placed in each box. During the experiment there was no observation

of leachate loss from the boxes. Each of five boxes was set up with a bottom layer of 25 mm washed gravel, a second layer of 150 to 200 mm of unsieved soil and a final layer of 15-18 cm of soil previously sieved through a 8 mesh screen (≤2.46 mm). For each specific dilution as shown in Table 2.1, the calculated proportion of creosote and topsoil were mixed to approximate the relative dilution from the 100% creosote box, as follows:

For example: 50% creosote box

- •unsieved layer — -0.22 m^3 of topsoil was mixed with 0.22 m^3 of creosote contaminated soil
  -the mixing was accomplished by tilling and turning the soil with a shovel and a hoe for a 15 minute duration
- •sieved layer — -0.22 m^3 of sifted soil was mixed as described above with 0.22 m^3 of sifted creosote soil
  -the sifting was accomplished by placing mixed unsifted soil on a 1.8 m x 1.2 m 8 mesh screen and sifting the soil through by hand using protective gear

The logic of the top soil layer to be sieved was to maximize homogeneity of the soil and the PAH contaminant of concern. The second unsieved soil layer and the bottom layer of gravel was to have an increase of soil porosity with the increase of soil depth to mimic field conditions.

The four creosote contaminated boxes were housed in one of the environmentally controlled greenhouse rooms in the University of Alberta Biological Science Building Phytotron while the control box was placed in a similar separate room. According to

Atmospheric Environment Service, 10 hours of daylight per day would mimic a typical Alberta growing season day (Environment Canada, 1982, 1982b). With the experiment being carried out in winter with decreased hours of daylight, the rooms were equipped with sodium lamps to extend the length of daylight to 10 hours. Also, to control the temperature in the greenhouse, hotwater pipes were installed to maintain temperatures between 18 to 25°C.

The three types of vegetation used in the growth experiment were : carrots (*Daucus carota*, cv. avenger); lettuce (*Lactuca sativa*, cv. grand rapids leaf) and barley (*Horduem vulgare*, cv. duke). The individual species of vegetation were selected to insure species being genetically known and stable. Likewise, the possible exposure pathways of PAH uptake were used to select the types of vegetation. The lettuce was selected on the basis of its large leaf surface area and the increased probability of particulate air deposition. The carrot was chosen because of its relatively high lipid content (% by weight) and the possibility of comparing PAH uptake by the root peel and core. Barley was selected because of its physical dimensions (*i.e.* long stem and narrow leaves), its hardiness for growing in extreme conditions and its relevance as a forage crop for livestock.

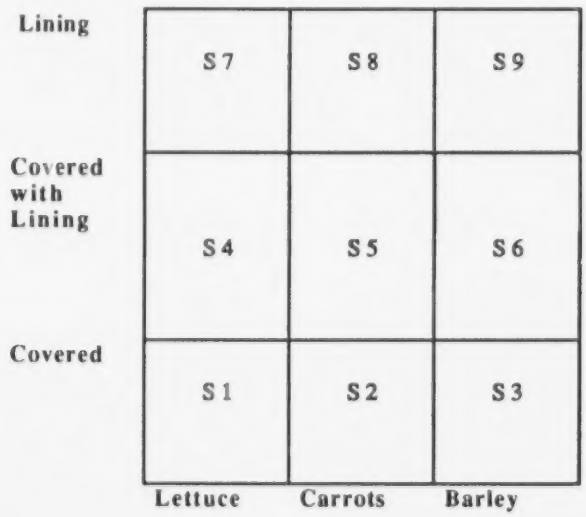
Three exposure pathways were investigated: particulate deposition, vapor transport and root uptake. These pathways were characterized by three exposure treatments: covered, lining and covered with lining.

The covered treatment refers to a polypropylene sheet forming a canopy over the plants which functioned to block air deposition from the greenhouse air that was in open contact with creosote contaminated soil. The second treatment, lining, refers to a polypropylene sheet (with 20 mm holes spaced 50 mm apart) that lined the surface of the soil. This lining functioned to block volatile PAHs from the soil migrating upward and

Table 2.1 Creosote Contaminated Soil Greenhouse Experimental Design

Proportion of Creosote Contaminated Soil	Covered Lettuce/ Carrots/ Barley	Lining Lettuce/ Carrots/ Barley	Covered with Lining Lettuce/ Carrots/ Barley
100%			
50%			
15%			
1%			
Control (Topsoil)			

A schematic diagram is given below to show the division of each box for the experiment (Figure 2.1):



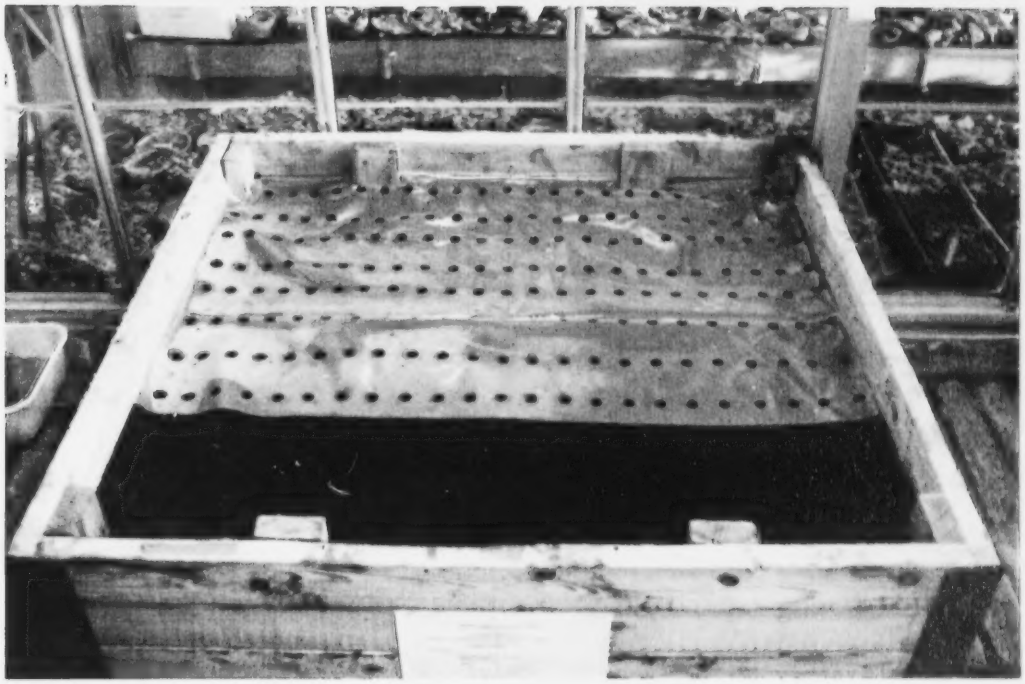


Figure 2.2. Greenhouse Experiment Setup

absorbing to the plant foliage. The treatment covered with lining refers to the combination of the first and second variable. All exposure conditions involved direct exposure of the plant roots to the PAHs in the contaminated soil and soil water.

Because the soil contained high levels of residual oil, soil hydrophobicity slowed the time (15 days) required for the boxes to reach at least a 25% moisture content in the higher creosote contamination levels. Once this 25% level was reached, the lining was placed and secured and the seeds were sown. The moisture content was measured by sampling the soil at random locations within each box and calculating percent moisture loss based on the difference of wet and dry weight of the soil sample. The estimated growth period for carrots, lettuce and barley were 60 to 80 days; 40 to 60 days and 40 to 50 days respectively. The official start date of the greenhouse experiment was December 11, 1992 and the termination date was April 22, 1993, a growth season of 132 days compared with an Alberta average of

90 days. The growth period was extended an additional 42 days because of the limited plant yields of lettuce and carrots in the higher contamination levels.

2.1.2 Borradaile On-site Growth Experiments

The on-site growth experiment was conducted at a former petroleum processing facility at Borradaile. This site had previously been evaluated for potential human health risk by Concord (1991). Because of limited data gathered from the site and with the estimated risk being unacceptable, growth experiments were performed to measure the PAH levels in soil and vegetation grown on-site. These PAH levels will then be used (Chapter 3) to assess the validity of the upper bound risk estimates known as base estimate case.

The Borradaile site is located 10 km east of Vermilion, north of Highway 16. An oil refinery was in operation at the site from 1942 to 1958. The refinery utilized a skimming operation to remove light fractions and heavy crude was disposed to unlined earthen pits. When the refinery was shut down in 1958, heavy crude in the pits was covered over with trees and straw and then backfilled.

The process plant at Borradaile was situated on a northeast side of the property above the slough that runs northwest-southeast along the railway lines (Figure 2.3). Across the slough to the east and along the stretch of railway line, the land rises gradually to a hill about 1.5 km north of the site. North of this is a series of ponds in a mixed shrub/agriculture terrain. The saline slough along the railway tracks is part of a series beginning at least 15 km to the west and north. Pipelines from the process plant site lead down to a loading area east of this first slough. The present condition of the site shows protruding pipes from the

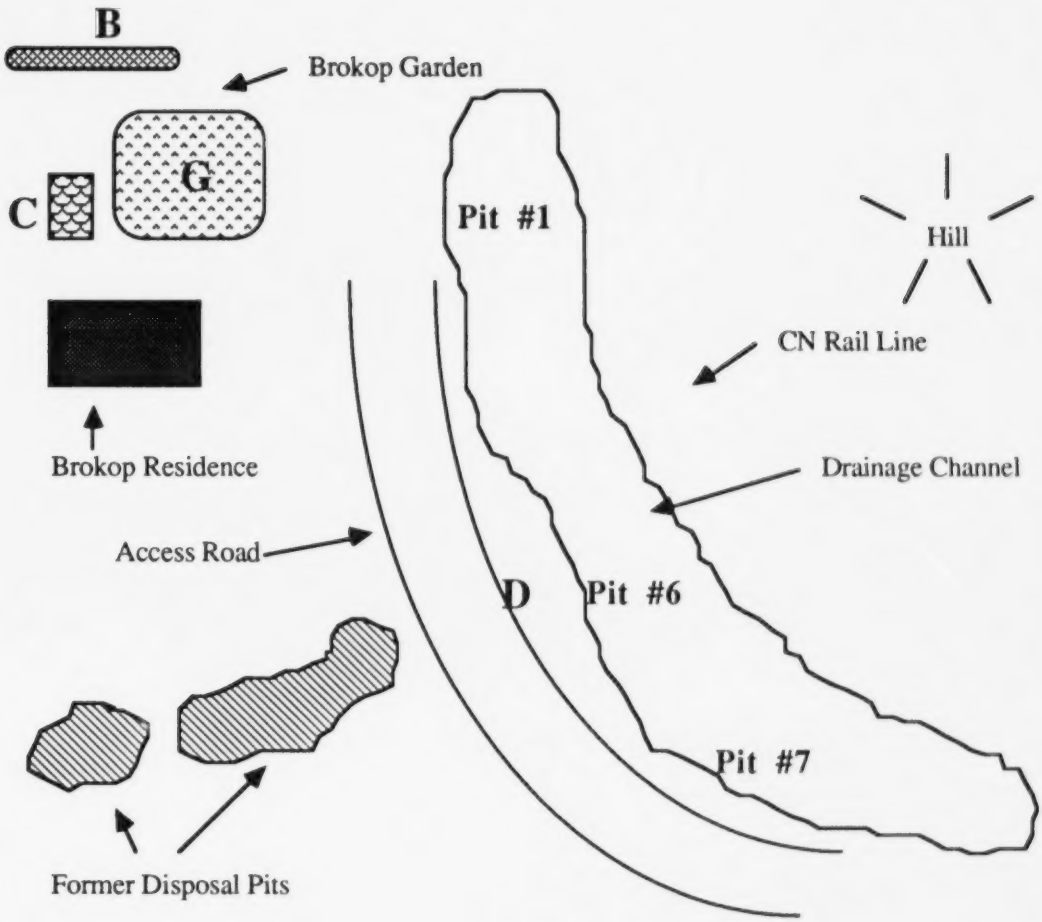


Figure 2.3 Map of the Borradaile Site (Schematic - not to scale)

ground and puddles of oily tar. About one kilometre downstream the slough drains under the railway and gradually directs to the north. The slough continues north for about one kilometre then turns east and returns south back across the railway. Oil was spilled into the north-western end of the slough that parallels the railroad from the loading area.

Other possible routes of oil leakage may have occurred or are still occurring through the pipelines running from the process area near the Brokop house under the road to the loading area. Oil from the disposal pits east of the Brokop house is travelling east, downhill under the gravel road to the slough referred to as Pit #6. The oil now extends about 600 m along the slough and has seeped under the railway and a further 150 m into the field (Figure 2.3).

Figure 2.4. Pit #6 and Drainage Channel

Figure 2.5 Garden Site

Four sites were selected for the growth experiment based on preliminary data from Pollard and Hrudey (1992). The garden site, designated site G (Figure 2.3) was composed of sand and silt with scattered debris of asphalt from the refinery operations. The intersect of the former disposal pits to the drainage channel was the location of the second contamination level. This site, designated as site D (drainage channel site), had a higher composition of clay and silt than that of the site G. The background level site (site B) was at the northwest edge of the Brokop's property. The control (site C) was comprised of non-contaminated soil from another location, the west side of the property . All the boxes in which the plants were grown were placed strategically, so the highest contamination was downwind from the other boxes.

2.1.2.1 Experimental Design

The experimental set-up consisted of a total of 16 cedar boxes with the dimensions of 1.2 m x1.2 m with a depth of 0.6 m. There were four boxes for each of the levels of soil contamination; control (C site), background (B site), garden site (G site) and drainage channel (D site). Each box was filled with the first 25 mm layer consisting of washed 25 mm gravel for necessary water drainage. The second layer comprised of 0.3 m unsieved soil for that specific site and the final layer of 0.3 m of soil was sifted through a 8 mesh screen (≤ 2.46 mm pore size) to ensure contaminant homogeneity. The set-up of the soil layers was to closely mimic soil zones found at a field site with the increase of soil porosity with depth. Water was added to each box to allow the soil to reach a 25% moisture content for immediate seedling growth response. The moisture content was measured by sampling the soil at random locations within each box and calculating percent moisture based on the difference of wet and dry weight of the soil sample. Each of the levels were treated identically to minimize the variability of the experiment.

The types of vegetation used in the growth experiment are described in the Creosote contaminated soil greenhouse experiment section.

The basic design of the experiment was similar to the creosote contaminated soil greenhouse experiment. In a general overview, particulate deposition, vapor transfer and root uptake were three possible exposure pathways to the vegetation considered in this study. The four boxes were designated open, lettuce, carrot and barley. The open box was divided into three equal sections and planted with seedlings of carrot, lettuce and barley. The other three boxes, which were designated for each of the three vegetation types to be grown, were also divided into three sections defined by three treatments differentiating the three mentioned pathways: covered, lining and covered with lining. The covered treatment, refers to a

polypropylene sheet overtop of the plants which functioned to block external aerosol deposition. The second treatment lining, refers to a polypropylene sheet that lined the surface of the soil with slits for the plant shoots to grow.

Table 2.2. Borradaile Field Experimental Design

Contamination Sites	Carrots 1. Covered 2. Covered with lining 3. Lining	Barley 1. Covered 2. Covered with lining 3. Lining	Lettuce 1. Covered 2. Covered with lining 3. Lining	Open Carrots Barley Lettuce
Site G				
Site D				
Site C				
Site B				

This lining functioned to block volatile PAHs and soil splashing from absorbing into the plant foliage. The treatment, covered with lining, refers to the combination of the first and second treatment. All exposure conditions allowed direct exposure to the PAHs in the contaminated soil and soil water.

Once the soil reached a 25% moisture content, the seeds were sown 10 mm below the soil surface in a grid pattern, covered with soil and water lightly. The estimated growth period for carrot, lettuce and barley were 60 to 80 days, 40 to 60 days and 40 to 50 days, respectively. The start date for the experiment was July 20, 1992. Collection of meterological data (*i.e.* temperature, precipitation), monitoring growth, water requirements and compiling a photograph log was made biweekly. Temperature maximum and minimum data for the length of the experiment were collected from Environment Canada - Climate Services. The overall average temperature range was 25° C to 0°C. Growth was slow for the

control (site C), background (site B) and the garden site (site B) because of the difficulty in maintaining a constant moisture content in the soils. In addition, the late start in the growing season and the two major cold snaps in late August (min. -9°C with heavy snowfall) and early September stunted the growth process (Environment Canada, 1982a). Therefore, the growth period for the vegetation was extended from the original intended harvest date of September 18, 1992 (60 days) to October 3, 1992 (75 days).

In addition to the vegetation experiment, various plants from the site were collected, identified and analyzed for PAHs (Figure 2.3).

Area of sampling	Species of vegetation
Pit #7	*Triglochin maritima*
Pit #6	*Salicornia rubra A. nels. /Hordeum jabatum L.*
Pit #1	*Hordeum jabatum L.* (wild barley)

2.1.3 Sample Collection and Preparation

Each of the three sections of each box was divided in two therefore each of the boxes was actually divided into six sections. Each of the three exposure conditions included each of the three plant species. Soil samples were collected from each of the sections at the start of the experiment before seeding and at the termination of the experiment after harvesting the vegetation. The samples were collected at the approximate depth of the root system (70 to 80 mm) for each of the three species of vegetation. The samples were placed in borosilicate jars which were previously acid washed. The soil samples were transported in coolers packed with dry ice and then they were stored in a 4°C cold room until processing. The longest period for sample storage before subsequent analysis was approximately 30 days.

The plants were harvested over a three day period. The harvesting strategy was to collect individual and composite samples for each of the sections (Kratochvil *et al.*, 1986). The barley and lettuce samples were separated into root and foliage. The root systems for each plant were cleaned meticulously with distilled/deionized water before being bagged in ziploc polypropylene bags and stored in a freezer at -20°C. The foliage was bagged unwashed and was stored at -20°C. The carrots were also cleaned with distilled/deionized water and then separated into root peel and root core using a kitchen peeler (peel ≤1 mm thick). Measurements of plant yield (based on wet weights), height of foliage and length of roots were made. From each of the 16 boxes, six composite and 27 individual plants were collected and separated into foliage and root components. The individual samples were collected based on wet weight. Two to three barley plants were collected per section because there was a small weight yield per plant. One lettuce sample was sufficient per section because of the large weight yield per plant. The composite samples were the remaining vegetation after the individual samples were collected, ranging from 8 to 15 plant samples.

2.1.4 Analytical Methods

2.1.4.1 Soil Sample Extraction and Cleanup

A 4 to 5 g sample of sieved soil was weighed into a Whatman Soxhlet thimble, pre-extracted with double distilled dichloromethane for 3 hours. At this stage a deuterated surrogate standard solution containing deuterated naphthalene-d_8 acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12} and perylene-d_{12} at a concentration of 5 µg/mL was added. The soil was then extracted for 16 hours with 150 mL of dichloromethane on a Soxhlet extractor. The extracts were concentrated to 5 mL by means of a rotary evaporator (Brinkmann, model# 131612) and quantitatively transferred to glass vials. The volumes

were then reduced to 1 mL under N_2 blowing. Cleanup of the extracts was performed by passing them through a 6 g Sep-Pak Florisil cartridge (Supelco) and rinsing the cartridge with 30 mL of dichloromethane. The volumes were then reduced to 1 mL under N_2 blowing and the solvent was exchanged to hexane. The resulting extracts were chromatographically cleaned by alumina according to the EPA Method 3611A.

Each chromatographic column was prepared by placing approximately 10 g of alumina into a 300 mm x 15 mm glass column with a teflon stopcock and approximately 1.5 g of anhydrous sodium sulfate to the top of the alumina. The column was washed with 50 mL of hexane and this solvent was discarded. Just prior to exposure of the sodium sulfate to the air, the sample extract was applied to the top of the column and eluted with 15 mL of hexane which was discarded. The column was then eluted with 100 mL of dichloromethane, yielding a fraction containing the base/neutral aromatics. This fraction was reduced to a final volume of 5 mL in a graduated test tube. The internal standard, a solution of anthracene-*d10* in dichloromethane was added before analysis by gas chromatography/mass selective detector (GC/MSD).

2.1.4.2 Plant Sample Extraction and Cleanup

Each of the plant samples was freezed-dried before extraction. Samples were prepared by first homogenizing the frozen vegetation in a food blender (lettuce), Turrax homogenizer (barley) and coffee grinder (carrots). Various instruments were used for homongenization because the barley was too fibrous to disrupt the plant to the cellular level with a blender and the carrots have a small composite size. Once the samples were homogenized, shell freezing was performed to allow efficient freeze drying. Shell freezing was accomplished by rotating the liquid extract contained in a round bottom flask, in an

acetone/dry ice bath until forming an inner shell on the flask wall. The freeze dryer (Labconco 4.5 with a Trivac "A" Dual Stage Rotary Vane Pump) was operated at temperatures reaching below -50°C and a pressure below 100 microns. When all the frost had disappeared from the outer surface of the sample container and cold spots were not detected by handling the container, the sample was found to be dry.

The freeze-dried vegetation samples were weighed and transferred into Soxhlet extractors pre-rinsed with dichloromethane with glass wool at the bottom outlet to prevent any plant debris entering the bottom flask. The samples were extracted for 24 hours and then reduced with the rotary evaporator to 5 to 7 mL. The extracts were transferred to glass vials and concentrated to 1 mL under a stream of nitrogen. Two stages of sample cleanup were performed. The first followed EPA Method 3620A, involving Florisil chromatography to remove lipids and chlorophyll. The second followed EPA Method 3611A, involving alumina chromatography for the separation of the petroleum wastes into aliphatics, aromatics and polar fractions.

The Florisil was activated to a 100% activity by heating the adsorbent to 450° C for 2 to 3 hours in a muffle furnace and then allowing it to cool in a dessicator. For insuring PAH recovery, a standard run was carried out for each Florisil batch. A specific concentration of deuterated standard was eluted through the Florisil at a given plant sample to quantify the recoveries. At 100% activation, the PAHs were retained on the column. It was shown that 5% deactivation of the Florisil gave better recovery of the PAHs. Along with the samples, the associated quality control samples-blanks were processed through this cleanup procedure. Deactivation was performed by adding a certain volume of deionized water to a given amount of 100% activated Florisil. A 5% deactivation was obtained by adding 2.5 mL of water to 50 g of Florisil. Overnight mixing was performed

by placing the mixture on the rotary evaporator in a round bottom flask and the adsorbent was used the next day.

For the first stage of the plant extract cleanup 5 g of 5% deactivated Florisil in a 300 mm x 15 mm column was sufficient for the removal of chlorophyll and lipid content typically found in lettuce and barley. The column was prepared by placing 5 g of Florisil into a glass column partially filled with dichloromethane. After the Florisil settled, approximately 1.5 g of anhydrous sodium sulfate was added to the top of the column. The column was conditioned with 50 mL of dichloromethane. The 1 mL sample extract was applied to the column and an additional 1 to 2 mL of dichloromethane was used to complete the transfer. Elution was performed with 100 mL of dichloromethane into a 250 mL flat bottom flask. The eluate was concentrated by a stream of nitrogen to 1 mL.

The plant cleanup procedure with alumina (EPA Method 3611A) was identical to that used for the soil analysis.

2.1.4.3 Air Monitoring

Standard procedures for air sampling of PAHs have been issued by the National Institute for Occupational Safety and Health. The NIOSH Method 5515 uses a personal air sampler in conjunction with an adsorbent tube. The ORBO adsorption tubes complies with all NIOSH specifications for tube dimensions, adsorbent quality and particle size, divider composition and pore size. The typical tube is divided into two adsorbent beds. The front section is twice the size of the back section. The back section is a backup section to determine if break through of airborne contaminants occurred on the front section.

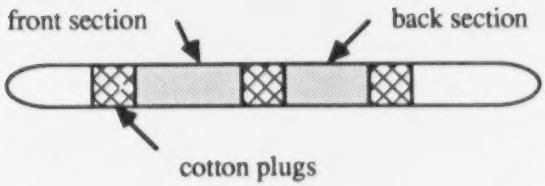


Figure 2.6 XAD resin tube

As with most synthetic polymers used for adsorbents, measurable or perhaps significant quantities of one or more of the following types of chemical contamination can occur: residual monomers; artifacts of the polymer synthesis process (*e.g.* byproducts); chemical preservatives to inhibit chemical or biological degradation.

Amberlite XAD resins are synthetic adsorbents structurally comprised of a styrene-divinylbenzene copolymer. Because of the polymeric synthesis process, users are cautioned that these resins do contain significant quantities of preservatives and monomers as received from the manufacturer. GC/MS consistently confirmed the presence of significant concentrations of a variety of aromatic hydrocarbons including alkylated derivatives of benzene, styrene, naphthalene and biphenyl. In the case of the ORBO tubes it was stated by Supelco that the tubes have been washed, however blanks runs would be necessary to verify this claim and the amount of interference this would cause to the analysis. Quality control blank runs were processed through the preparation procedure to check for any interferences.

Procedure:

Because of the low turbulence within the greenhouse, the airborne particulates were low and only the adsorbent tube was used inline with the ALPHA-1 Constant Flow Air Sampler. The recommended flow rate had been advised to be 2L/min, however due to

the absence of an in-line filter the flow rate was reduced to approximatelly 1.5L/min Before each run the air sampler was calibrated to ensure desired flowrate.

To desorb the sorbent from the tube, the front section and the glass wool was transferred into one culture tube, while the back section (only sorbent) was transferred to a second culture tube. To each culture, 5 mL of toluene was added and capped. The samples were held for 30 min and occasionally mixed. All samples were filtered through an 0.45 μm membrane filter. To each culture a deuterated standard solution of 5 μg/mL was added to calculate recoveries.

2.1.4.4 Oil and Grease (Solvent Extractable Residue)

The method for oil and grease was a modified version of the soxhlet extraction method from Standard Methods (APHA-AWWA-WPCF, 1989). The method involved weighing a given soil sample and placing it in a soxhlet extraction thimble with Na_2SO_4 to absorb any water in the soil sample. The thimbles were previously oven dried at 103°C for 30 min. The extraction flask was also weighed. Extraction of the oil and grease was done in the soxhlet apparatus with 150 mL of dichloromethane at a rate of 20 cycles/hr for 6 hrs. The solvent in the apparatus was completely drained into the extraction flask and placed in the fumehood to allow the solvent to evaporate. The flask was placed in the dessicator for 1 hr and then removed and weighed. Based on weight differential of the extraction flask divided by the original soil sample weight, a concentration based on dry weight was calculated.

2.1.4.5 Instrumentation - Thermal Desorption/GC/MS and GC/MS

Two methods of instrumental analysis were used in the series of sample analysis in this study:

2.1.4.5.1 Thermal Desorption

Thermal desorption analysis was carried out by Marv Rawluk of the Alberta Research Council based in Edmonton, Alberta.

A Ruska Laboratories ThermEx pyrocell was interfaced to the GC/MS described below. A known amount (typically 15 to 25 mg) of soil or plant plus spiked deuterated homocyclic PAHs were placed in the pyrocell and thermally desorbed at a linear heating rate of 30°C min^{-1} from 50°C to 280°C, then 4°C min^{-1} to 300°C with cryogenic focussing. The gas chromatograph (Carlo Erba HRGC 5160) oven temperature was kept at 35°C until thermal desorption was complete. Chromatography of the thermally extracted material was then performed by heating the DB-5 column (0.32 mm x 25 m, 0.25µm film thickness, fused silica capillary from 35°C to 310°C at a linear temperature gradient of 10°C min^{-1}. A Finnigan Matt 4500 mass spectrometer was operated in a mutiple ion detection MID) electron impact (EI) mode. A total scan time of 2.2 seconds was employed. The ion source temperature was 150°C and the electron multiplier operated at 1150V. The corresponding electron impact energy was 70eV.

2.1.4.5.2 Gas Chromatography/Mass Spectrometry

The indentification of PAHs were obtained by using a GC/MS employing a Hewlett-Packard Model 5890 gas chromatograph coupled to a Hewlett-Packard Model

5970 mass selective detector. Conditions were as follows: DB 1301 column, 30 m long, 0.251 mm ID, 0.25 μm film thickness. Helium was the carrier gas and the linear velocity was approximately 400 mm/s. Splitless injection was 1 μL. The injection was at 280°C and the detector was at 280°C, autotuned. The oven was programmed with an increase of temperature at 10°C/min up to 280°C after a 4 min of initial hold time at 70°C. The temperature was then increased at 20°C/min up to 300°C and kept at that temperature for 5 min, for a total run time of 48 min. The mass selective detector conditions were as follows: acquisition mode- selective ion monitoring (SIM); electron impact 70eV; electron multiplier of 2400 V.

Full scan GC/MS were run for standard solutions to determine separation conditions, retention times, and major peaks to be used in the SIM mode. The full scan chromatograms provided good sensitivity and clean profiles, by the proper selection of the windows for the various groups of ions and dwell times of 100 ms for the monitored ion. For each sample run, three ions were monitored for each compound, the calculations being based on the most intense peak. The other two peaks were used for confirmation procedures in cases of interferences.

2.2 Results and Discussion

The level of confidence in site characterization and strategies to deal with hazard waste sites is directly dependent on the quality and reliability of data analysis methodologies. Conventional analytical techniques require considerable sample cleanup and sophisticated interpretation which make them costly for extensive evaluation. More reliable and cost effective screening techniques are being implemented (Junk *et al.*, 1991). Recently, thermal extraction techniques have been investigated as a rapid alternative to classical soil analysis by solvent extraction followed by GC/MS.

Thermal desorption followed by GC/MS (TD/GC/MS) and Soxhlet extraction followed by GC/MS were two methods selected for soil and plant analysis at Borradaile. Thermal desorption offers a fast and safe alternative to classical extraction procedures for a wide range of semi-volatile pollutants (Robbat *et al.*, 1992). In this technique, ground or homogenized samples are loaded into porous quartz crucibles with little preparation. Analytes are volatilized at a preprogrammed temperature profile and subsequently cryocondensed onto a conventional gas chromatographic column. The detection of individual PAHs can then be performed using conventional gas-chromatograph mass spectrometry. Priority PAH pollutants present in the Borradaile site soil and vegetation samples were identified by corresponding retention time relative to deuterated standards and their mass spectra. Analytes are normally thermally desorbed under reducing conditions to prevent pyrolysis and/or oxidation.

The Soxhlet extraction method requires a wet solvent extraction followed by two selected column cleanup procedures, Florisil and alumina. Florisil is a magnesium silicate used to separate aromatic compounds from aliphatic-aromatic mixtures and to remove

waxes and chlorophyll (EPA, 1982). The alumina column has better resolving capability to separate the aromatic compounds from the "base/neutral" aliphatics and polar compounds.

A comparison of the thermal and solvent extraction procedures was undertaken using Certified Standard Reference Material (SRM) and specific Borradaile plant and soil samples. Both methods were optimized independently. Different column temperature programming were used along with different tuning parameters for the mass spectrometer. The overall thermal extraction efficiencies for the SRM (HS-3 and HS-6) did not appear to be better than soxhlet extraction efficiencies. The recoveries were found to vary considerably between the two methods. Table 2.3 shows a slightly higher thermal desorption effeciency for the low molecular weight PAHs (naphthalene - chrysene) and a relatively lower recovery for the other PAHs (benzo(b,k)fluoranthene - benzo(g,h,i)perylene), as compared to those obtained with Soxhlet extraction. Also noted was a decrease in the recoveries obtained where analyte concentrations were lower.

Results of the thermal desorption of the Borradaile plant and soil samples are presented in Tables 2.4 and 2.5 and the Soxhlet extraction results in Table 2.6, 2.21 and 2.22. The thermal desorption values are based on triplicate analysis while the Soxhlet extraction values are based on duplicate analysis. The vegetation results with thermal desorption varied considerably to the soxhlet extraction results. The reasons for this is probably the small sample size used for analysis and the heterogeneity of the vegetation sample. The soil sample results with Soxhlet extraction were more consistent. The soils generally reported higher values for the low molecular weight PAHs. Pollard and Hrudey (1992), have shown that the variability in the extraction methods is matrix dependent. The recoveries are found to be dependent on polarity, molecular weight and analyte matrix (Pollard and Hrudey, 1992).

Table 2.3 Soxhlet Extraction and Thermal Desorption Recoveries of Two Standard NRC Reference Sediments

PAHs	NRC Reference Soil HS-3					NRC Reference Soil HS-6				
	NRC Conc. (µg/g)	Soxhlet Recovered Conc A (µg/g)	Thermal Desorption Conc B. (µg/g)	Soxhlet Recovery (%)	Thermal Desorption (%)	NRC Conc. (µg/g)	Soxhlet Recovered Conc A	Thermal Desorption Conc B.	Soxhlet Recovery (%)	Thermal Desorption (%)
Naphthalene	9.0	8.3±0.2	12.6±1.2	92.7	139.4	4.1	4.5±0.08	9.5	110.7	231.7
Acenaphthylene	0.3	0.7±0.03	3.4±0.5	245.5	1133.3	0.2	0.4±0.02	2.0±0.6	235.7	1070.2
Acenaphthene	4.5	4.2±0.2	5.9±0.6	93.3	130.4	0.2	0.2±0.01	0.2±0.06	66.1	104.3
Fluorene	13.6	11.1±0.4	11.4±0.5	81.3	83.6	0.5	0.3±0.03	0.7±0.3	73.7	144.7
Phenanthrene	85.0	83.4±1.3	83.6±4.5	98.1	98.4	3.0	3.8±0.08	3.8±0.7	127.1	125.6
Anthracene	13.4	8.0±0.4	23.3±0.3	60.0	173.6	1.1	1.3±0.06	3.7±0.7	115.2	336.4
Fluoranthene	60.0	84.9±2.8	59.4±3.2	141.5	99.0	3.5	6.4±0.1	3.5±0.4	180.2	97.9
Pyrene	39.0	20.7±0.7	41.3±1.8	53.1	105.9	3.0	2.1±0.4	3.1±0.3	70.2	103.3
Benzo(a)anthracene	14.6	16.1±0.1	16.9±0.9	110.6	116.0	1.8	2.0±0.5	2.3±0.2	109.9	125.9
Chrysene	14.1	9.6±0.3	13.7±0.5	68.0	97.2	2.0	2.3±0.3	2.4±0.2	116.6	118.3
Benzo(b,k)fluoranthene	10.5	13.1±0.9	8.1±0.6	124.3	76.8	4.2	4.8±0.1	2.8±0.2	114.6	66.2
Benzo(a)pyrene	7.4	5.3±0.2	7.8±0.6	72.1	105.0	2.2	1.8±0.1	2.8±0.4	83.0	125.8
Indeno(1,2,3,-cd) pyrene	5.4	7.0±0.7	3.0±0.3	128.7	54.9	2.0	2.2±0.2	1.2±0.1	114.8	63.2
Dibenzo(a,h)anthracene	1.3	1.7±0.2	0.8±0.1	134.2	61.3	0.5	0.7±0.08	0.3±0.04	143.5	55.8
Benzo(ghi)perylene	5.0	4.8±0.4	6.5±1.7	95.9	13.0	1.8	1.6±0.2	2.7±0.2	92.5	153.6

Table 2.4. PAH Analysis of Borradaile Vegetation by TD/GC/MS (μg/g)

	Borradaile Vegetation					
Sample ID	Site G Carrot Peel	Site G Lettuce	Site G Lettuce	Site G Barley	Site G Barley	Site G Barley
naphthalene	no	no	no	no	no	no
acenaphthylene	no	no	no	no	no	no
acenaphthene	no	no	no	no	no	no
fluorene	no	no	no	no	no	no
phenanthrene	nd	nd	nd	nd	nd	0.38
anthracene	nd	nd	0.60*	nd	nd	nd
fluoranthene	0.14	0.08	0.07	nd	0.08	0.06
pyrene	0.25	0.05	0.08	nd	0.19	0.16
benzo(a)anthracene	0.09	0.04	nd	0.02	0.07	0.03
chrysene	0.07	0.02	nd	0.03	0.09	0.09
benzo(b)fluoranthene						
benzo(k)fluoranthene	nd	nd	nd	nd	nd	nd
benzo(e)pyrene	nd	no	no	no	no	no
benzo(a)pyrene	nd	nd	nd	nd	nd	nd
perylene	nd	nd	nd	nd	nd	nd
indeno(1,2,3,-cd) pyrene	nd	nd	nd	nd	nd	nd
dibenzo(a,h) anthracene	nd	nd	nd	nd	nd	nd
benzo(ghi)perylene	nd	nd	nd	nd	nd	nd

nd = not detected (<0.01 ppm)
no = not obtainable (concentration <1ppm) due to coeluting compounds
* value probably elevated due to coeluting compound

* Analysis by Marv Rawluk of Alberta Research Council

Table 2.5 PAH Analysis of Borradaile Soil by TD/GC/MS (μg/g)

	Borradaile Soil					
Sample ID	Site G Carrot	Site G Lettuce	Site G Lettuce	Site G Barley	Site G Barley	Site G Barley
naphthalene						
acenaphthylene	0.01	0.02	0.03	0.02	nd	nd
acenaphthene	nd	nd	0.03	0.02	0.01	nd
fluorene	0.05	nd	0.04	0.14	0.10	nd
phenanthrene	0.02	0.04	0.04	0.16	0.03	0.04
anthracene	0.09	0.10	0.08	0.49	0.14	0.08
fluoranthene	0.09	0.11	0.07	1.8	0.42	0.31
pyrene	0.09	0.14	0.09	1.4	0.38	0.30
benzo(a)anthracene	0.03	0.07	0.04	0.30	0.09	0.07
chrysene	0.03	0.09	0.05	0.30	0.09	0.08
benzo(b)fluoranthene						
benzo(k)fluoranthene	0.01	0.05	0.02	0.09	0.03	0.02
benzo(e)pyrene	0.01	0.05	0.02	0.07	0.03	0.02
benzo(a)pyrene	nd	0.03	0.01	0.08	0.02	0.01
perylene	0.08	0.07	0.04	0.05	0.07	0.05
indeno(1,2,3,-cd) pyrene	nd	0.03	0.02	0.06	nd	nd
dibenzo(a,h) anthracene	nd	nd	nd	nd	nd	nd
benzo(ghi)perylene	nd	0.06	0.03	0.59		0.01

nd = not detected

detection level≤ 0.005 μg/g

Table 2.6. PAH Analysis of Borradaile Vegetation by GC/MS-Soxhlet Extraction (μg/g dry wt.)

	Borradaile Vegetation					
Sample ID	Site G Carrot	Site G Lettuce	Site G Lettuce	Site G Barley	Site G Barley	Site G Barley
naphthalene	0.024	0.032	0.070	0.031	0.063	0.035
acenaphthylene	nd	nd	nd	nd	0.001	nd
acenaphthene	0.005	0.005	0.016	0.003	0.006	0.004
fluorene	0.003	0.003	0.014	0.003	0.002	nd
phenanthrene	0.009	0.016	0.048	0.018	0.017	0.011
anthracene	0.002	0.014	0.018	0.003	0.003	0.002
fluoranthene	0.003	0.032	0.020	0.013	0.007	0.006
pyrene	0.005	0.025	0.013	0.006	0.014	0.004
benzo(a)anthracene	nd	0.006	nd	0.004	0.003	nd
chrysene	nd	0.010	nd	0.006	0.007	nd
benzo(b)fluoranthene						
benzo(k)fluoranthene	nd	nd	nd	nd	nd	nd
benzo(a)pyrene	nd	nd	nd	nd	nd	nd
indeno(1,2,3,-cd) pyrene	nd	nd	nd	nd	nd	nd
dibenzo(a,h) anthracene	nd	nd	nd	nd	nd	nd
benzo(ghi)perylene	nd	nd	nd	nd	nd	nd

nd = not detected

Recent studies at the Borradaile site have shown that for Borradaile soils, dichloromethane was a poor extractant for PAH components. This was demonstrated by the recovery of PAHs by thermal desorption from soil pre-extracted with dichloromethane (Pollard and Hrudey, 1992). The issue of extraction efficiency is also related to the availability of contaminants and is a key element often overlooked in risk assessment. Low extraction efficiencies observed for higher molecular weight PAHs may be due to their lack of availability in the bulk solution. Micropores of individual soil aggregates may not be large enough to allow PAHs to move freely and be in continual contact with the solution. Lower molecular weight PAHs have a tendency to desorb off soils to a greater extent and at a faster rate than higher molecular weight PAHs, which may be due to size and solubility. Thus extraction efficiency is dependent on the availability of the contaminant in the bulk solution which is rate limited by the desorption/diffusion process. In the case of the Borradaile soil matrix, the finer texture and slightly increased clay content was at least partially responsible for the binding of PAHs to the soil and resulting poor extraction recoveries (Pollard and Hrudey, 1992). The extraction recoveries for creosote soils with the soxhlet extraction method was found to be efficient with high percent recoveries (Pollard and Hrudey, 1992). The creosote used in the comparison of extraction efficiencies was also used for the greenhouse growth experiment.

The level of oil and grease (O&G) for each of the creosote levels used in the greenhouse experiment are presented in Table 2.7. The O&G levels correspond well to the intended percent creosote levels. The initial PAH concentrations in each of the creosote experimental boxes are summarized in Table 2.8. The total PAH concentration was from 3580 ± 172 (100%) to 23.2 ± 2.41 (1%) µg/g on a dry weight basis (DW). The control box contained a low PAH content, 0.15 ± 0.031 µg/g DW. Table 2.9 shows the final PAH concentrations of the creosote contaminated soil at each of the dilutions. Figure 2.7 shows that PAH concentrations decreased substantially by 60 to 80% by the end of the

growth period , except for the control which had decreased by only 30%. A closer investigation on the concentration variation of specific PAHs shows that the 3- and 4-ring compounds experienced the most drastic reduction (Figure 2.8 to 2.12). The 3-ring compounds consist of: acenaphthene; acenaphthylene; anthracene; phenanthrene and fluorene. The group of 4-ring compounds include: fluoranthene; benz(a)anthracene; chrysene and pyrene. The 3- and 4-ring PAH are the largest proportional constituents of creosote (Mueller *et al.*, 1989), as can be seen in Table 2.8 and Figures 2.8 to 2.12.

In all the boxes the highest ring number and highest molecular weight PAHs, such as benzo(a)pyrene, dibenz(a,h)anthracene, benzo(g,h,i)perylene and indeno(1,2,3-c,d)pyrene appeared to be the most persistent. The changes in surface layer PAHs ranged from less than 15% for the 5- and 6-ring PAHs compared to 70 to 90% decreases for the 3- and4-ring PAHs.

Table 2.7 Oil and Grease Content of Creosote Contaminated Soil Greenhouse Experiment

	Oil and Grease (µg oil/g dry soil)	
Creosote Levels	Mean	SD
100%	45300	600
50%	23700	500
15%	7200	300
1%	1300	200
Control	100	

Table 2.8 Initial PAH Concentrations of Creosote Contaminated Soil at each Dilution (µg/g dry wt basis)

Sample Identification	100%	50%	15%	1%	Control
2-ring					
naphthalene	11.7 (0.6)	9.83 (0.75)	4.71 (0.90)	0.16 (0.033)	0.010 (0.0001)
3-ring					
acenaphthylene	nd	nd	nd	nd	nd
acenaphthene	336 (21)	217 (25)	64.7 (2.2)	1.99 (0.24)	0.037 (0.002)
fluorene	316 (11)	195 (20)	63.1 (0.2)	2.35 (0.17)	0.028 (0.005)
phenanthrene	738 (18)	520 (5)	160 (5)	4.47 (0.12)	
anthracene	682 (15)	383 (62)	147 (0)	5.45 (1.35)	0.050 (0.008)
4-ring					
fluoranthene	707 (88)	435 (97)	167 (1)	4.71 (0.14)	0.014 (0.004)
pyrene	431 (7)	358 (33)	98.8 (1.0)	2.13 (0.22)	0.007 (0.004)
benzo(a)anthracene	51.0 (3.0)	42.8 (6.5)	7.95 (0.42)	0.24 (0.005)	
chrysene	118 (2)	74.1 (5.1)	25.0 (0.3)	0.79 (0.070)	0.004 (0.0003)
5-ring					
benzo(b+k)fluoranthene	111 (0)	85.8 (10.5)	24.9 (0.3)	0.64 (0.035)	0.002 (0.0005)
benzo(a)pyrene	44.3 (1.0)	33.6 (2.3)	8.63 (0.24)	0.25 (0.015)	nd
dibenzo(a,h)anthracene	2.82 (0.64)	2.83 (0.77)	1.30 (0.21)	0.023 (0.005)	nd
6-ring					
indeno(1,2,3,-cd)pyrene	14.8 (0.6)	13.6 (0.8)	3.23 (0.040)	0.12 (0.005)	nd
benzo(ghi)perylene	15.8 (0.4)	15.1 (2.2)	4.14 (0.52)	0.012 (0.00)	nd

{SD} = Standard Deviation of a triplicate analysis.

Table 2.9 Final PAH Concentrations of Creosote Contaminated Soil at each Dilution (μg/g dry wt. basis)

Sample Identification	100%	50%	15%	1%	Control
2-ring					
naphthalene	11.9 {1.2}	7.90 {1.06}	1.20 {0.54}	0.12 {0.03}	0.004 {0.002}
3-ring					
acenaphthylene	1.42 {0.05}	0.62 {0.02}	<0.001 {0}	<0.001 {0}	<0.001 {0}
acenaphthene	20.3 {1.9}	6.74 {2.06}	0.91 {0.33}	0.060 {0.001}	0.002 {0.001}
fluorene	24.8 {1.5}	12.8 {2.8}	2.35 {1.29}	0.10 {0.02}	0.004 {0.001}
phenanthrene	55.0 {1.7}	33.1 {4.8}	6.31 {2.92}	0.31 {0.03}	0.019 {0.004}
anthracene	162 {19}	75.6 {20.7}	18.0 {15.7}	0.54 {0.18}	0.004 {0.001}
4-ring					
fluoranthene	250 {3}	47.1 {3.2}	5.91 {1.54}	0.53 {0.06}	0.006 {0.001}
pyrene	364 {4}	49.5 {4.4}	3.38 {1.09}	0.51 {0.17}	0.005 {0.001}
benzo(a)anthracene	62.6{0.6}	11.4 {0.3}	1.36 {0.39}	0.15 {0.03}	0.002 {0.001}
chrysene	94.5 {4.4}	21.7 {2.9}	2.60 {0.63}	0.26{0.02}	0.003 {0.001}
5-ring					
benzo(b+k)fluoranthene	70.6 {22.2}	35.95{1.4}	2.94 {0.75}	0.45 {0.08}	0.003 {0.002}
benzo(a)pyrene	51.8 {1.2}	17.8 {1.1}	1.65 {0.33}	.26 {0.05}	<0.001 {0}
dibenzo(a,h)anthracene	16.2 {0.3}	3.07 {0.15}	0.32 {0.05}	0.057 {0.011}	0.001 {0}
6-ring					
indeno(1,2,3,-cd)pyrene	13.2 {1.2}	13.2 {0.3}	1.40 {0.18}	0.26 {0.06}	0.003 {0.002}
benzo(ghi)perylene	14.9 {1.1}	11.8 {0.3}	1.23 {0.16}	0.23 {0.05}	0.001 {0}

{SD} = Standard Deviation of a triplicate analysis.

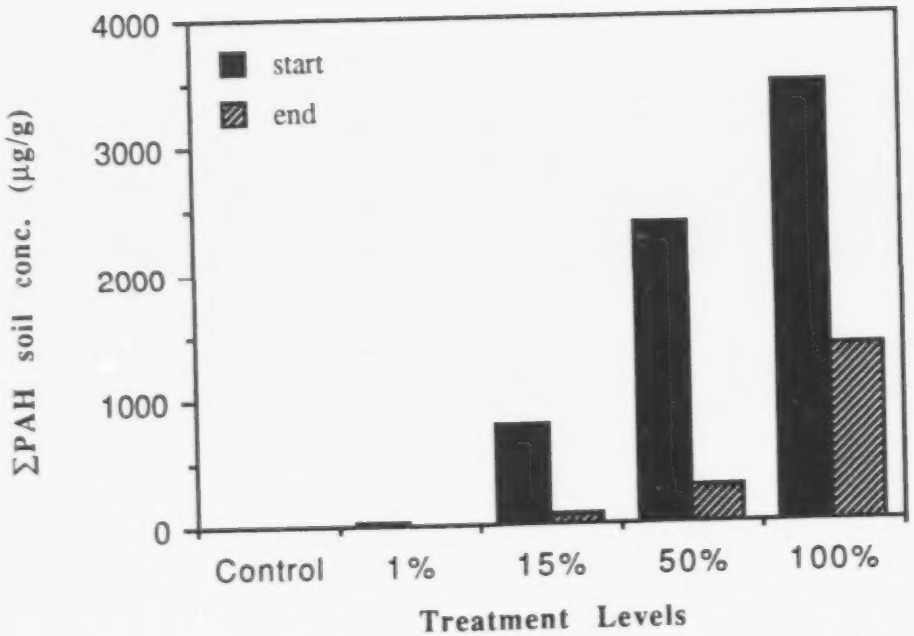


Figure 2.7. Initial and Final Soil PAH Concentrations (µg/g) Detected in each Treatment Level.

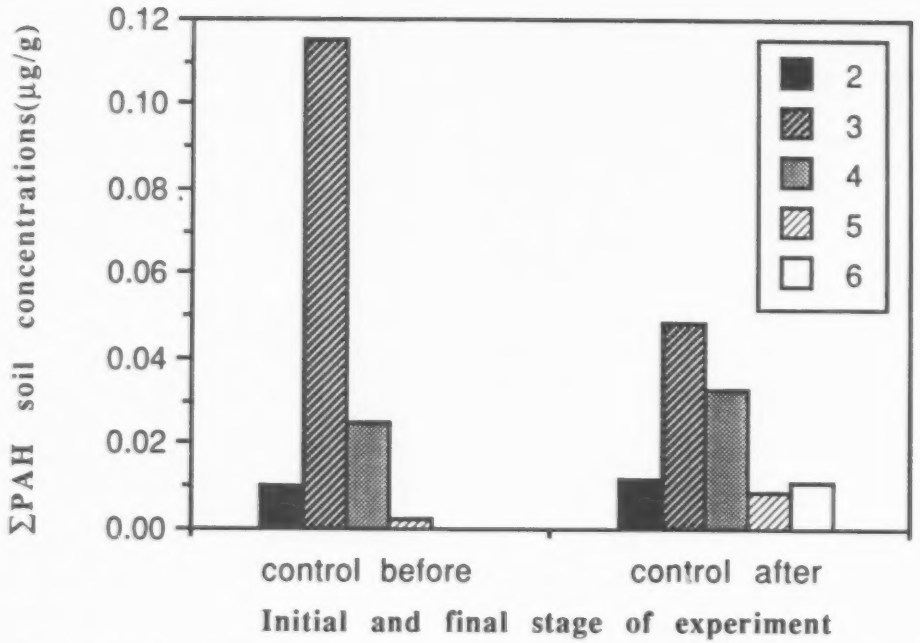


Figure 2.8. Initial and Final Soil Concentrations for each of the PAH Ring Classes for the Control Level.

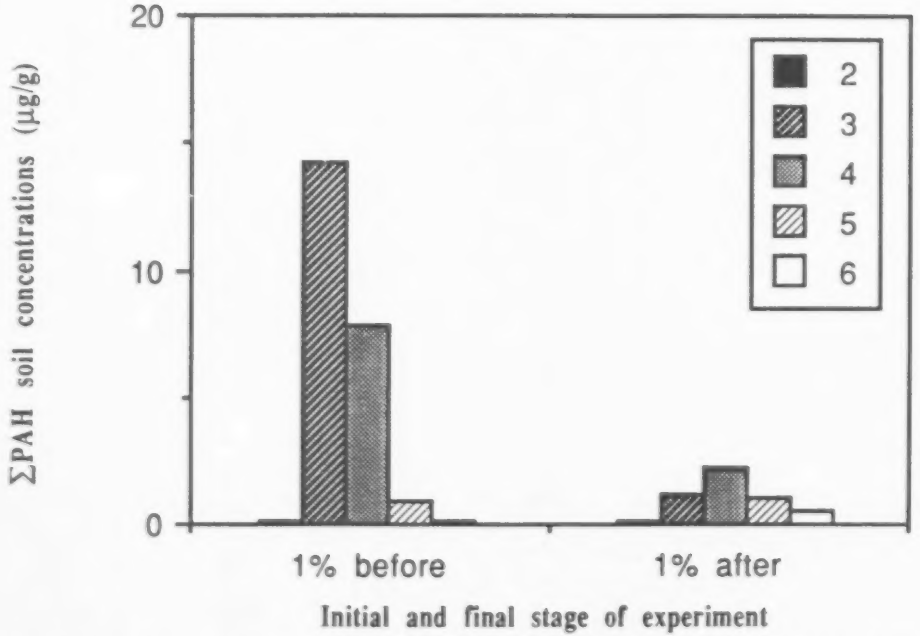


Figure 2.9. Initial and Final Soil Concentrations of each of the PAH Ring Classes for the 1% Creosote Level.

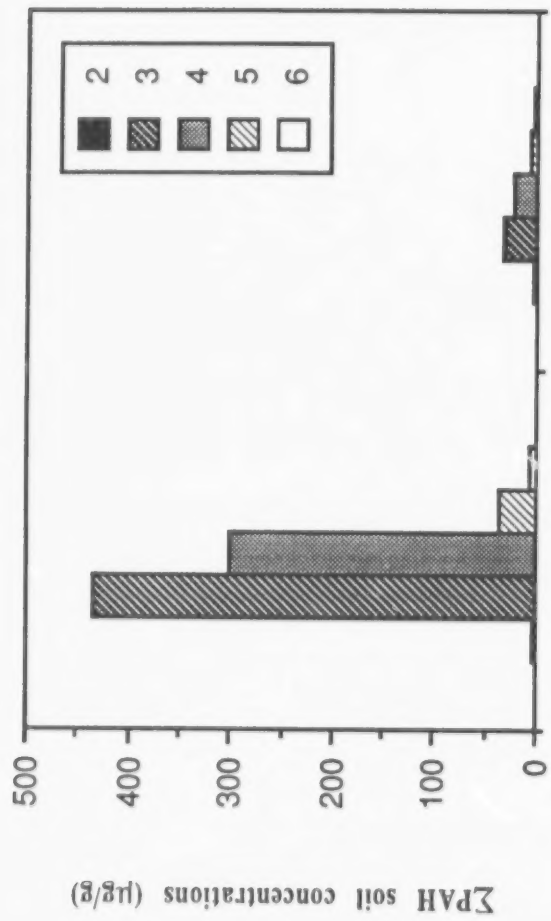


Figure 2.10. Initial and Final Soil Concentrations for each of the PAH Ring Classes for the 15% Creosote Level.

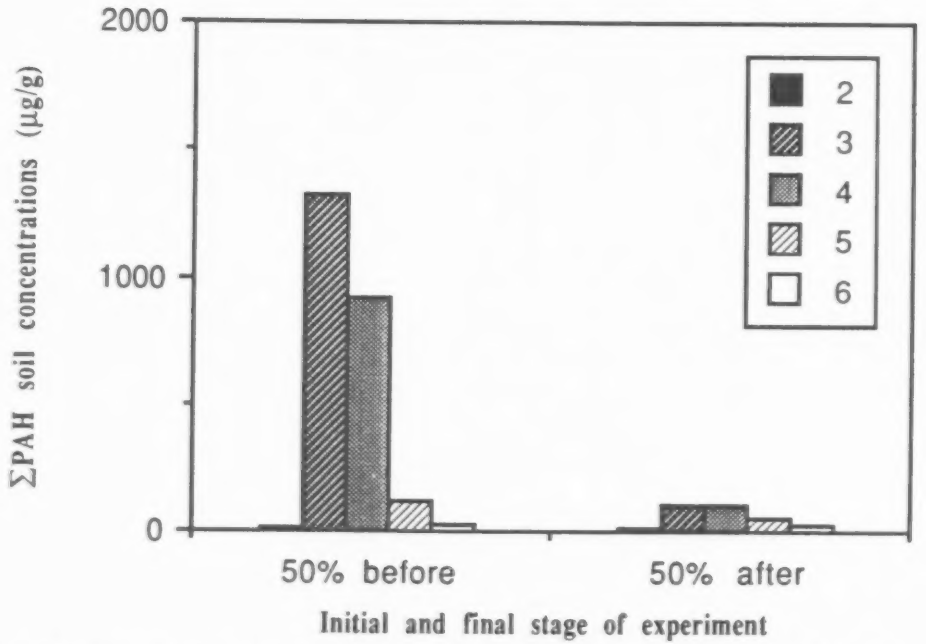


Figure 2.11. Initial and Final Soil Concentrations for each of the PAH Ring Classes for the 50% Creosote Level.

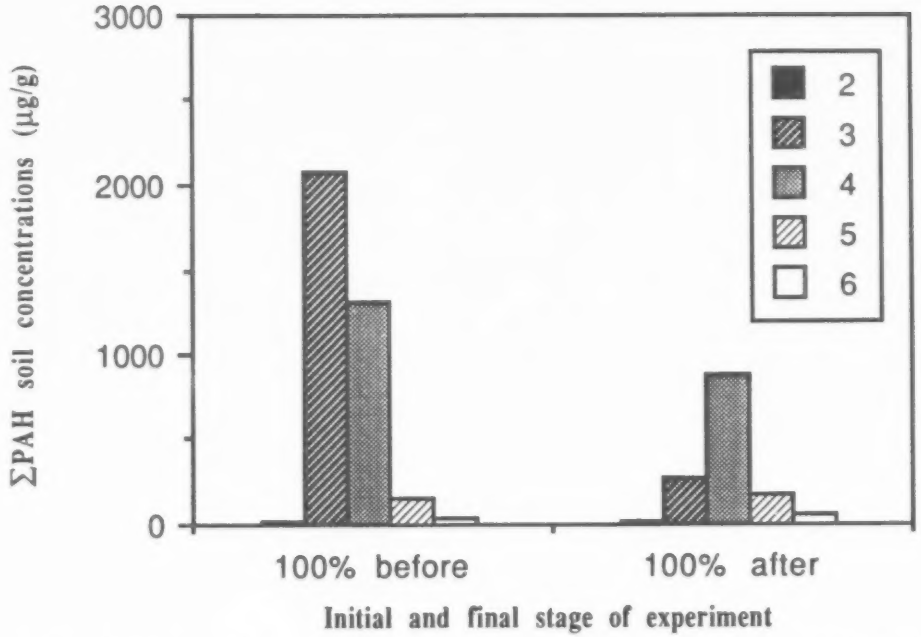


Figure 2.12. Initial and Final Soil Concentrations for each of the PAH Ring Classes for the 100% Creosote Level.

Air monitoring was performed to monitor the PAH levels in the greenhouse throughout the growth period. The four PAHs- naphthalene, phenanthrene, pyrene and benzo(a)pyrene were selected and monitored over a period of 20 weeks. As expected, the PAHs with low vapor pressure, such as benzo(a)pyrene, was in the lowest abundance (Figure 2.14). Levels show a dramatic decrease in January. This is due to the addition of the covers to the experiment boxes, enclosing the sections (Figure 2.13). The PAH levels after this point indicate that air particulate deposition was not a dominant factor in foliar uptake.

The persistence or loss mechanisms of creosote components are dependent on the physico-chemical properties of each of the specific PAHs and the combining effects in such a complex mixture. Abiotic degradation (photolysis and hydrolysis), volatilization, biological oxidation and leaching are four environmental fate mechanisms influencing PAHs in the environment.

PAHs are susceptible to abiotic degradation such as photodegradation and hydrolysis. However, under the conditions of this experiment, photodegradation and hydrolysis were not independently assessed. Destruction mechanisms including abiotic and biotic processes are more important for the PAHs when photodegradation is controlled (Park *et al.*, 1990a). Recent literature suggests that under abiotic conditions, losses of 2- and 3-ring PAH compounds from soil are predominant (Park *et al.*, 1990a, 1990b and Wild *et al.*, 1991a). Under controlled conditions, Park et al (1990b) have shown 1.8 to 17.4% abiotic loss of 2- and 3-ring PAH compounds in bioinhibited soil. Naphthalene is usually lost by volatilization, however the larger molecular weight PAHs, 3- and 4-ring compounds, are also prone to this process. Table 2.8 and 2.9 show minor losses of naphthalene but, extensive losses of 3- and 4-ring compounds.

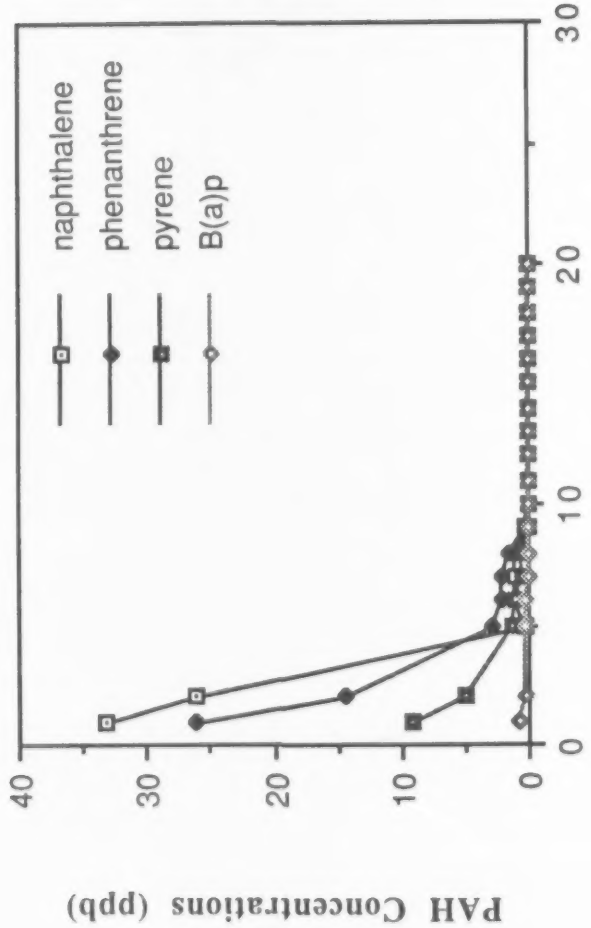


Figure 2.13. PAH Air Concentrations in the Greenhouse from January - May 1993.

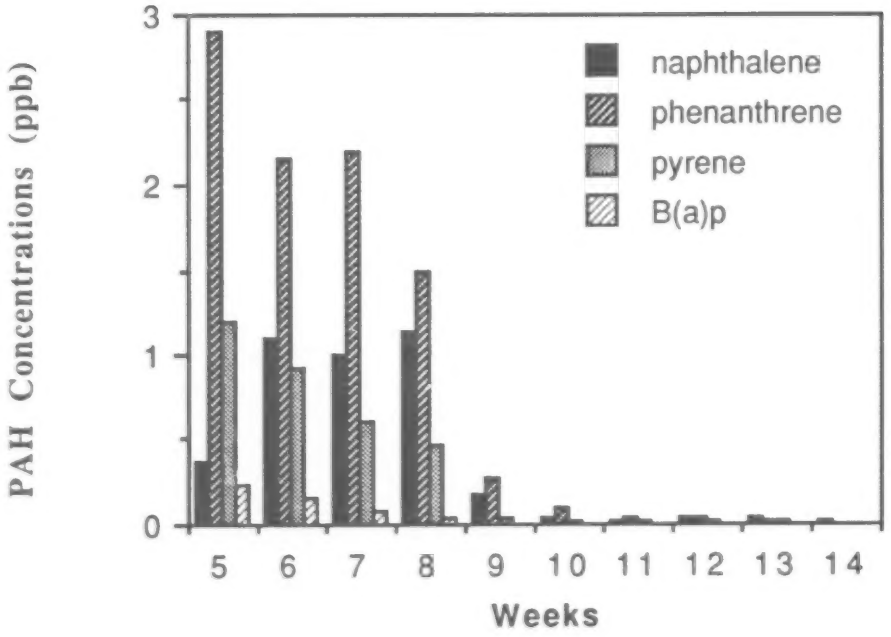


Figure 2.14. PAH Air Concentrations in the Greenhouse from Week 5 to 14.

The higher molecular weight and ring class PAHs were more persistent as reported in other studies (Bossert *et al.*, 1984 and Sims and Overcash, 1983).

Increased soil temperature has also been reported to significantly increase the rate of loss of low molecular weight PAHs, but had little effect on the 5- and 6-ring PAHs (Coover and Sims, 1987). For PAHs compounds with more than 4 rings neither volatilization nor abiotic mechanisms played a significant role in removal. Studies show 2- and 3-ring PAH compounds to be biotransformed extensively in soil systems. This transformation of PAH compounds was negatively correlated with their molecular weight or number of fused rings (Park *et al.*, 1990b).

Higher water content in the soil may also increase volatilization by creating an air convection current from water evaporation that will enhance movement and loss of volatiles to the surface of the soil. Consequently, PAH concentrations increase at the soil surface under evaporating conditions and the volatilization rate increases with time (Ryan et al., 1988). This process will allow for an increased soil to air volatilization and subsequent sorption to plant foliage and PAH loss to the atmosphere.

PAHs are hydrophobic compounds and tend to bind strongly to soil particles, primarily soil organic matter. Sorption of nonionic compounds is strongly dependent on the organic content as well as the nature of the organic matter in the soils (Grathwohl, 1990). Sorption has been an important factor used to determine the fate of PAHs in water/soil systems. A positive linear relationship exists between PAH concentrations and organic matter content (Karickhoff *et al.*, 1978 and Means *et al.*, 1980). Sorption is also referred to as partitioning and is often described by a partition coefficient, K_p (Mackay, 1991). From the linear partition coefficient K_p and the organic content of the sorptive substrate (creosote soil), a sorption constant, K_{oc}, can be determined. The K_{oc} is related to

the solubility of a compound and the octanol-water partition coefficient, K_{ow}. Studies have shown significant linear relationships between log values of both water solubility and K_{ow}, and the corresponding sorption constants, K_p, when normalized for organic carbon (Means *et al*, 1980). The K_{ow} values for PAHs are high and therefore PAHs have a high tendency to bind to soil organic carbon (Mackay, 1991).

Leaching is directly dependent on the sorptive capacity of a compound to the organic matter in the soil. In the experiment, the level of organic carbon in the treatment boxes ranged from 4.07 to 6.56 %. Because of the hydrophobicity in the 100% and 50% creosote treatment level, water channeling was observed to flow below the vadose zone (root area) to the bottom of the box, which allowed for rapid water flow and may have resulted in leaching. Table 2.10 shows an increase of 3- and 4-ring PAH compounds at the bottom of the boxes compared to the PAH soil concentrations shown at the beginning of the experiment (Table 2.8). The leaching process may have increased the level of 3- and 4-ring compounds from soil samples analyzed from the bottom of the box, with little variation of naphthalene. Generally, for the lower treatment levels, leaching losses were small in terms of the overall mass balance.

The soils from the Borradaile Site had low, but detectable levels of PAHs. The PAH behavior for the creosote contaminated soil was similar to the Borradaile soils. Overall, the higher molecular weight PAHs were shown to be more recalcitrant than the low molecular weight PAHs.

Biodegradation is an important and likely loss mechanism for some of the PAHs. A common cited observation is that the more soluble, low molecular weight PAH compounds are generally biodegraded at a faster rate and to greater extent than the less

Table 2.10 Creosote PAH Levels at Bottom of Treatment Boxes - Leaching (µg PAH/ g dry wt soil)

Sample Identification	100%	50%	15%	1%
2-ring				
naphthalene	11.0	8.97	4.23	0.15
3-ring				
acenaphthylene	1.00	0.50	<0.001	<0.001
acenaphthene	420	296	67.7	2.09
fluorene	418	235	64.1	2.48
phenanthrene	802	681	182	4.92
anthracene	774	369	162	6.01
4-ring				
fluoranthene	787	495	182	5.21
pyrene	438	362	102	2.41
benzo(a)anthracene	53.6	43.1	8.11	0.23
chrysene	119	76.1	27.3	0.78
5-ring				
benzo(b+k)fluoranthene	116	87.2	27.1	0.62
benzo(a)pyrene	45.1	34.6	9.79	0.26
dibenzo(a,h)anthracene	3.41	3.11	1.26	0.05
6-ring				
indeno(1,2,3,-cd)pyrene	16.2	13.8	3.54	0.19
benzo(ghi)perylene	14.5	15.1	4.05	0.16

soluble, higher molecular weight PAHs. Lower biodegradation rates observed for 5- and 6-ring compounds may be due to lack of bioavailability (Smith *et al*, 1989). The micropores of soil aggregates may be large enough for chemicals to desorb and diffuse into the aqueous solution, but the microorganisms may be too large to enter these pores. Therefore, bacteria require a combination of adsorption/desorption and diffusion of the organic contaminant into the aqueous phase. The higher molecular weight PAHs have a high log octanol/water partition coefficient (log K_{ow}) (Table 1.2) and are present in the residual oil or to the organic fraction in the soil, which renders them less available for biodegradation, leaching and volatilization.

This theory also relates PAH structure with degradation rates being inversely proportional to the number of fused rings in the compound (Sims and Overcash, 1983). Studies have shown increasing degradation rates for recalcitrant 4- and 5-ring PAHs when the soil was mixed with contaminated soil rather than with pristine soil, because of the presence of adapted microflora (Keck *et al.*, 1989). Because microorganisms cannot use 5- and 6-ring compounds as direct substrates, cooxidation is cited as an explanation.

From observations in this experiment, it is clear that the rate and extent to which PAHs are removed from soils is influenced by the combined and simultaneously occurring effects of processes such as volatilization, leaching and biological oxidation. Lower molecular weight PAHs are most likely influenced by biodegradation and volatilization, whereas higher molecular weight PAHs are probably controlled by biodegradation (Park *et al.*, 1990a). The large removal of 3- and 4-ring PAH compounds from surface soil might be explained by the high concentrations at the start of the experiment providing a greater potential for loss from the surface soil.

Yields of barley, lettuce and carrots on a fresh weight basis are presented in Table 2.11 and 2.12. There was no growth observed for barley and lettuce in the 100% creosote treatment level and no growth of lettuce in the 50% creosote treatment level. This could be explained by the toxic effect of creosote on these plants or effective water deficiency. Many of the water soluble and polar constituents (*e.g.* phenolic compounds) have been shown to be toxic to microorganisms using the Microtox assay (Symons *et al.*, 1988).

The foliage yields for barley and lettuce with the control were 209± 161 g and 338 ± 7 2 g respectively. Under each of the creosote modified treatment levels, the yields of both the foliage and roots were affected. In all of the treatment levels (100%, 50%, 15% and 1%), growing barley and lettuce produced less foliage than in the control. Plant growth declined with increasing amounts of creosote added in experiments done by Bossert and Bartha (1984). However, the opposite was observed for the carrots, with the low creosote application (1% and 15%) stimulating both foliage and root production (Table 2.12). Very low hydrocarbon levels (<1%) may actually stimulate plant growth and crop yield (Sims and Overcash, 1983).

In the case of the 50% treatment level, carrot root formation and development was suppressed (Figure 2.15). Other variables besides toxicity, such as high oil content and/or imbalance of moisture may be a factor for this result . The highest foliage and root yields were from the 1% and 15% treatment levels, with a 400% and 560% yield respectively, as compared to that in the control.

Chemical uptake and distribution within plants is affected by the physico-chemical properties of PAHs, the environment conditions, soil type and the plant characteristics such as root system, shape and chemical characteristics of the leaves and lipid content. Chemical uptake in plants is complex and may involve active and/or passive processes.

Table 2.11. Barley and Lettuce Yields (fresh harvested weight basis)

Sample	Mean Height of Plant (mm)	Mean Length of Roots (mm)	Mean Weight of Composite Plant/Section (g)	Mean Weight of Composite Roots/Section (g)
	Mean {SD}*	Mean {SD}*	Mean {SD}*	Mean {SD}*
CONTROL				
Barley	590 {60}	55 {39}	208 {161}	23 {6}
Lettuce	190 {30}	35 {13}	338 {72}	11 {4}
1 %				
Barley	334 {226}	13 {1}	224 {274}	23 {18}
Lettuce	247 {32}	83 {14}	169 {41}	9 {3}
15 %				
Barley	263 {35}	4.5 {0}	20 {14}	2.5 {2.2}
Lettuce	157 {32}	7.5 {0.5}	133 {36}	15 {3}
50 %				
Barley	330 {36}	40 {0}	13 {8}	4 {4}
100 %				
Barley	117 {84}	30 {0.3}	6 {4}	8 {1}

note: * {SD} = Standard Deviation, SD for the specified parameters were based on individual plant and root samples collected from each section (Figure 2.1) under each creosote level.

Table 2.12 Carrot Yields (fresh harvested weight basis)

Sample Identification	Composite Length of Carrot Foliage (mm)	Composite Weight of Carrot Foliage (fresh wt g)	Composite Weight of Carrot Peel (fresh wt g)	Composite Weight of Carrot Core (fresh wt g)
CONTROL				
Section 2	240	80.1	12.92	11.96
Section 5	290	133.0	20.80	19.58
Section 8	230	78.6	34.68	25.43
Mean {SD}*	253 {32}	97.2 {31.0}	22.80 {11.02}	18.99 {6.75}
1 %				
Section 2	360	284.8	103.84	93.61
Section 5	370	346.6	102.92	82.96
Section 8	350	266.5	70.72	55.38
Mean {SD}*	360 {10}	299.3 {42.0}	92.49 {18.86}	77.32 {19.73}
15 %				
Section 2	300	335.3	127.12	129.61
Section 5	270	279.1	97.72	112.41
Section 8	260	200.2	85.36	79.70
Mean {SD}*	277 {21}	271.5 {67.9}	103.40 {21.45}	107.24 {25.35}
50 %				
Section 2	210	131.4	20.12	12.99
Section 5	195	101.8	33.18	23.87
Section 8	180	72.4	32.83	26.10
Mean {SD}*	195 {15}	101.9 {29.5}	28.71 {7.44}	20.99 {7.01}

note: * {SD} = Standard Deviation, SD for the specified parameters were based on the three sections (Figure 2.1) under each creosote level for composite foliage, root core and root peel samples collected

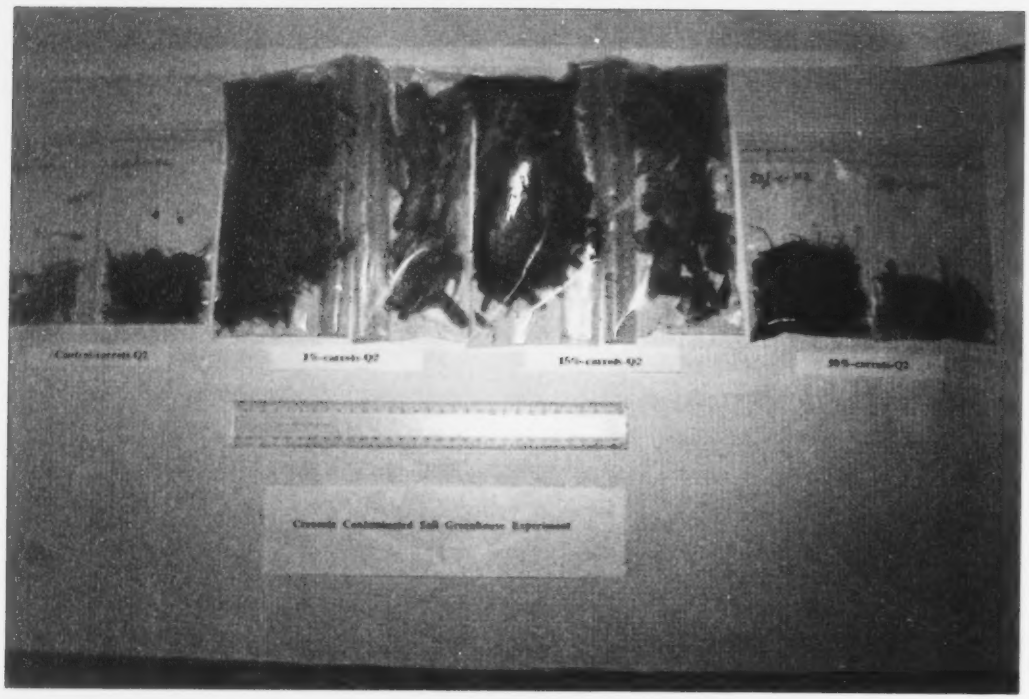


Figure 2.15. Photograph of Carrots Yields

This study had three treatments in place to assess the exposure pathways of sorption of volatiles from the soil, air deposition of volatiles and the root translocation of PAHs. In the greenhouse experiment the covered treatment was used to minimize air-particulate deposition. The lining treatment was used to suppress exposure to volatiles from the soil, while the covered with lining treatment was used as a combination to investigate root translocation of PAHs. For the discussion, the treatments- covered, covered with lining and lining will be abbreviated as summarized in Table 2.13.

Table 2.13 Abbreviation of Variables and Expected Exposure

Abbreviation	Experimental Conditions	Expected Exposure Allowed
L-RA	Lining	root uptake air-leaf deposition
C-RV	Covered	root uptake soil vapor uptake
C/L-R	Covered with Lining	root uptake only

Figure 2.16 shows the PAH levels in barley for each of the three treatments, C-RV, C/L-R and L-RA, under each of the 5 treatment levels. Experiments with C-RV shows a higher PAH load in the plant tissue than that for C/L-R and L-RA at all creosote levels, except 1% and the control. The PAH levels at the 1% level showed minimal differences between the exposure treatments (Table 2.14). The relative percent distribution of PAHs for each ring class in the barley plant in all the treatments were as follows:

3-ring compounds	7 to 18%
4-ring compounds	56 to 82%
5-and 6-ring compounds	8 to 17%

The PAHs responsible for the higher burden in the experiment with C-RV compared with C/L-R and L-RA were: fluoranthene, phenanthrene and anthracene (3-ring compounds) and benz(a)anthracene and chrysene (4-ring compounds). The higher values of these specific compounds may be due to their higher aqueous solubility and vapor

Table 2.14 Barley Grown in 100%, 50%, 15%, 1%, and Control Creosote Levels (µg PAH/g dry plant matter)

Sample Identification	100% covered S3 Barley	100% covered/ lining S6 Barley	100% lining S9 Barley	Standard Deviation (SD)	50% lining S3 Barley	50% covered/ lining S6 Barley	50% covered S9 Barley	Standard Deviation (SD)
2-ring								
naphthalene	0.51	0.12	0.27	(0.11)	0.13	0.03	0.09	(0.02)
3-ring								
acenaphthylene	0.31	0.41	0.45	(0.03)	0.09	0.10	0.07	(0.01)
acenaphthene	0.44	0.09	0.12	(0.02)	0.03	0.02	0.05	(0.02)
fluorene	0.45	0.16	0.14	(0.01)	0.09	0.06	0.27	(0.13)
phenanthrene	2.11	1.85	1.59	(0.18)	0.54	0.96	0.89	(0.23)
anthracene	1.19	0.53	1.31	(0.55)	0.32	0.53	1.58	(0.64)
4-ring								
fluoranthene	14.16	13.08	13.61	(0.37)	6.21	7.04	7.67	(1.65)
pyrene	18.19	14.71	10.38	(3.06)	3.11	5.67	7.54	(0.25)
benzo(a)anthracene	1.25	0.49	0.81	(0.22)	0.12	0.19	1.19	(0.47)
chrysene	5.36	3.13	3.91	(0.55)	0.57	0.81	3.08	(0.54)
5-ring								
benzo(b+k)fluoranthene	4.49	4.03	4.24	(0.15)	0.42	0.56	1.84	(0.26)
benzo(a)pyrene	1.87	1.07	1.40	(0.23)	0.10	0.18	0.52	(0.06)
dibenzo(a,h)anthracene	0.29	0.25	0.27	(0.01)	0.04	0.05	0.52	(0.02)
6-ring								
indeno(1,2,3,-cd)pyrene	1.27	0.85	0.97	(0.08)	0.14	0.23	0.46	(0.11)
benzo(ghi)perylene	0.79	0.77	0.86	(0.06)	0.14	0.23	0.40	(0.03)

(SD) = Standard Deviation was based on a triplicate analysis of the composite plant sample. From the three treatments for each percent creosote level, the treatment (*i.e.* lined)that produced the largest (SD) was reported for each section.

Table 2.14 Continued

Sample Identification	15% lining S3 Barley	15% covered/ lining S6 Barley	15% covered S9 Barley	Standard Deviation {SD}	1% covered S3 Barley	1% covered/ lining S6 Barley	1% lining S9 Barley	Standard Deviation (SD)
2-ring								
naphthalene	0.030	0.027	0.032	{0.010}	0.034	0.021	0.027	{0.007}
3-ring								
acenaphthylene	0.041	0.045	0.026	{0.005}	0.013	0.009	0.019	{0.003}
acenaphthene	0.034	0.010	0.013	{0.002}	0.026	0.017	0.007	{0.006}
fluorene	0.045	0.026	0.051	{0.021}	0.029	0.019	0.024	{0.008}
phenanthrene	0.240	0.130	0.160	{0.007}	0.150	0.120	0.082	{0.013}
anthracene	0.100	0.100	0.940	{0}	0.050	0.024	0.036	{0.007}
4-ring								
fluoranthene	0.660	0.480	0.660	{0}	0.260	0.240	0.340	{0.038}
pyrene	0.630	0.480	0.310	{0.091}	0.270	0.280	0.170	{0.028}
benzo(a)anthracene	0.027	0.011	0.019	{0}	0.009	0.008	0.005	{0.001}
chrysene	0.110	0.058	0.089	{0.001}	0.028	0.020	0.019	{0.001}
5-ring								
benzo(b+k)fluoranthene	0.290	0.089	0.180	{0.021}	0.005	0.004	0.004	{0}
benzo(a)pyrene	0.065	0.028	0.067	{0.005}	0.003	0.002	0.002	{0}
dibenzo(a,h)anthracene	0.026	0.015	0.033	{0.006}	0.001	0.001	0.004	{0.001}
6-ring								
indeno(1,2,3,-cd)pyrene	0.120	0.057	0.110	{0.014}	0.017	0.011	0.004	{0.001}
benzo(ghi)perylene	0.120	0.054	0.110	{0}	0.020	0.012	0.005	{0.001}

{SD} = Standard Deviation was based on a triplicate analysis of the composite plant sample. From the three treatments for each percent creosote level, the treatment (*i.e.* lined)that produced the largest {SD} was reported for each section.

Table 2.14 Continued

Sample Identification	Control covered S3 Barley	Control covered/ lining S6 Barley	Control lining S9 Barley	Standard Deviation {SD}
2-ring				
naphthalene	0.023	0.038	0.014	{0.007}
3-ring				
acenaphthylene	0.001	0.001	0.001	{0.0003}
acenaphthene	0.003	0.005	0.003	{0.003}
fluorene	0.004	0.005	0.004	{0.001}
phenanthrene	0.018	0.023	0.027	{0.004}
anthracene	0.004	0.005	0.003	{0.002}
4-ring				
fluoranthene	0.019	0.026	0.029	{0.002}
pyrene	0.037	0.063	0.077	{0.006}
benzo(a)anthracene	0.005	0.009	0.007	{0.002}
chrysene	0.007	0.012	0.017	{0.003}
5-ring				
benzo(b+k)fluoranthene	0.007	0.008	0.009	{0.003}
benzo(a)pyrene	0.004	0.012	0.009	{0.004}
dibenzo(a,h)anthracene	0.005	0.014	0.001	{0.002}
6-ring				
indeno(1,2,3,-cd)pyrene	0.006	0.012	0.001	{0.003}
benzo(ghi)perylene	0.006	0.014	0.010	{0.003}

pressure compared with 5- and 6-ring compounds (Wild and Jones, 1992a). This allows the volatiles from the soil to diffuse into the air phase and subsequently be taken up by the foliage. Topp *et al* (1986) showed that uptake by barley leaves *via* air was strongly positively correlated with volatilization of PAHs from the soil. For the semi-volatiles with a high log K_{ow}, translocation from the root system should be minimal. The increase for the 5- and 6-ring compounds in variable C-RV was most likely due to soil splashing because there was no protection with the lining. Soil splashing occurs during watering and maintenance of the growth boxes.

Experiment with L-RA showed levels of PAH uptake with all vegetation in all treatment levels (Table 2.14 and 2.15). In the case of C/L-R the predominance of PAHs were from the 3- and 4-ring compounds. Root translocation of the soluble PAHs may occur at a low level in conjunction with volatilization. Treatment L-RA allowed exposure to the air in the greenhouse and there was circulation of PAH vapors from the higher level boxes because a separate enclosed environments for each treatment were not available for these experiments. Therefore, the lining barrier was recognized as being unable to suppress the volatile exposure completely.

In Figure 2.17, the uptake of PAHs in barley in the greenhouse experiment was normalized by dividing by the corresponding soil concentrations. This figure shows that there is not a constant concentration factor between the plant concentration and the corresponding soil concentration at vegetation grown at varying soil PAH concentrations The correlations shown in Chapter 1 (RCF -equation 1 and SCF -equation 6), indicate that under varying soil concentrations the plant uptake concentration factor should be constant. Also, the overall results show that the plant/soil ratio (approximately 0.005 to 0.035) are generally low for these high soil PAH levels compared to plant/soil ratio (0.1 to 1.0) for the Borradaile low level soil PAH exposure (data in Table 3.24).

Table 2.15 Lettuce Grown in 15%, 1% and Control Creosote Levels (µg PAH/ g dry plant matter)

Sample Identification	15% lining S1 Lettuce	15% covered/ lining S4 Lettuce	15% covered S7 Lettuce	Standard Deviation {SD}	1% covered S1 Lettuce	1% covered/ lining S4 Lettuce	1% lining S7 Lettuce	Standard Deviation {SD}
2-ring								
naphthalene	0.089	0.024	0.150	{0.007}	0.022	0.022	0.019	{0.005}
3-ring								
acenaphthylene	0.028	0.012	0.045	{0.002}	0.004	0.004	0.007	{0}
acenaphthene	0.120	0.048	0.086	{0.001}	0.025	0.031	0.027	{0.001}
fluorene	0.077	0.033	0.210	{0.004}	0.014	0.013	0.016	{0.001}
phenanthrene	0.480	0.270	0.480	{0.042}	0.120	0.120	0.120	{0.001}
anthracene	0.150	0.098	0.550	{0.018}	0.018	0.017	0.016	{0.005}
4-ring								
fluoranthene	0.790	0.450	0.650	{0.13}	0.200	0.170	0.180	{0}
pyrene	1.07	0.560	0.790	{0.042}	0.170	0.130	0.160	{0.005}
benzo(a)anthracene	0.120	0.030	0.180	{0.015}	0.008	0.006	0.005	{0.001}
chrysene	0.310	0.050	0.380	{0.015}	0.018	0.013	0.013	{0}
5-ring								
benzo(b+k)fluoranthene	0.360	0.110	0.800	{0.021}	0.016	0.014	0.006	{0.004}
benzo(a)pyrene	0.200	0.055	0.410	{0.006}	0.007	0.007	0.003	{0}
dibenzo(a,h)anthracene	0.011	0.016	0.110	{0.006}	0.009	0.007	0.006	{0.003}
6-ring								
indeno(1,2,3,-cd)pyrene	0.180	0.058	0.400	{0.008}	0.015	0.007	0.006	{0.001}
benzo(ghi)perylene	0.060	0.058	0.400	{0.007}	0.009	0.009	0.004	{0.001}

{SD} = Standard Deviation was based on a triplicate analysis of the composite plant sample. From the three treatments for each percent creosote level, the treatment (*i.e.* lined)that produced the largest {SD} was reported for each section.

Table 2.15 Continued

Sample Identification	Control covered S1 Lettuce	Control covered/ lining S4 Lettuce	Control lining S7 Lettuce	Standard Deviation (SD)
2-ring				
naphthalene	0.018	0.017	0.020	(0.004)
3-ring				
acenaphthylene	0.001	<0.001	<0.001	(0)
acenaphthene	0.004	0.004	0.001	(0)
fluorene	0.003	0.003	0.004	(0)
phenanthrene	0.027	0.018	0.016	(0.0007)
anthracene	0.005	0.003	0.003	(0.0007)
4-ring				
fluoranthene	0.020	0.011	0.011	(0.001)
pyrene	0.029	0.021	0.030	(0.004)
benzo(a)anthracene	0.005	0.004	0.006	(0.003)
chrysene	0.007	0.004	0.006	(0.003)
5-ring				
benzo(b+k)fluoranthene	0.006	0.005	0.045	(0)
benzo(a)pyrene	0.003	0.003	0.007	(0.001)
dibenzo(a,h)anthracene	0.001	<0.001	0.004	(0)
6-ring				
indeno(1,2,3,-cd)pyrene	0.004	0.003	0.007	(0.005)
benzo(ghi)perylene	0.004	0.008	0.008	(0.001)

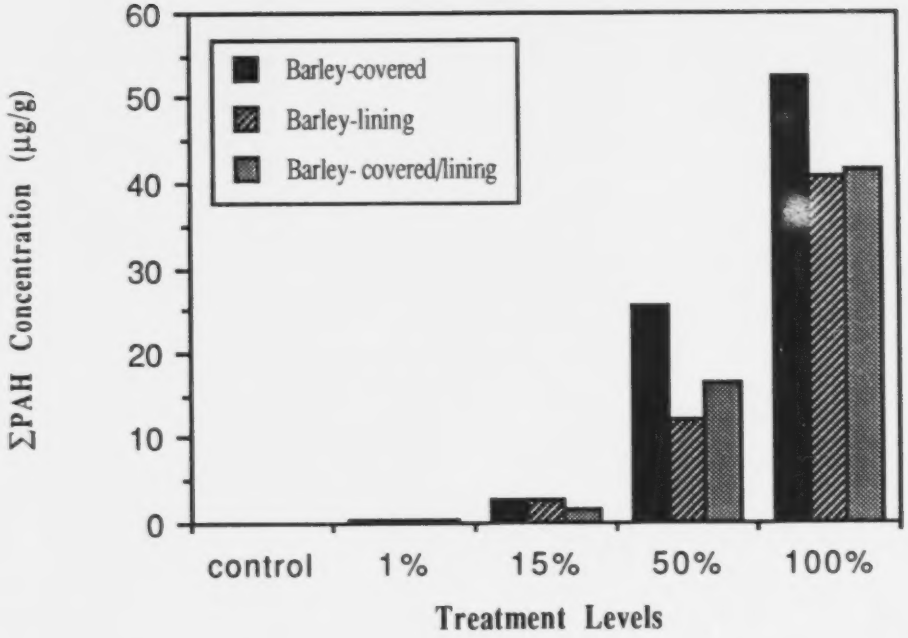


Figure 2.16. Barley: Percent Creosote Levels versus Experimental Treatments.

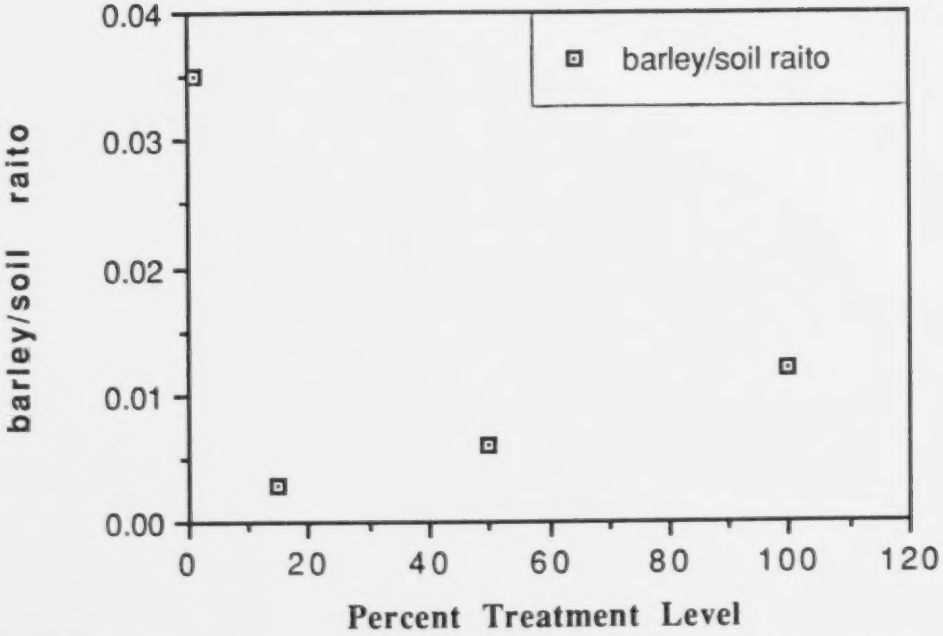


Figure 2.17. Barley Vegetation "Normalized" - ratio of barley PAH concentrations divided by the corresponding soil PAH concentration.

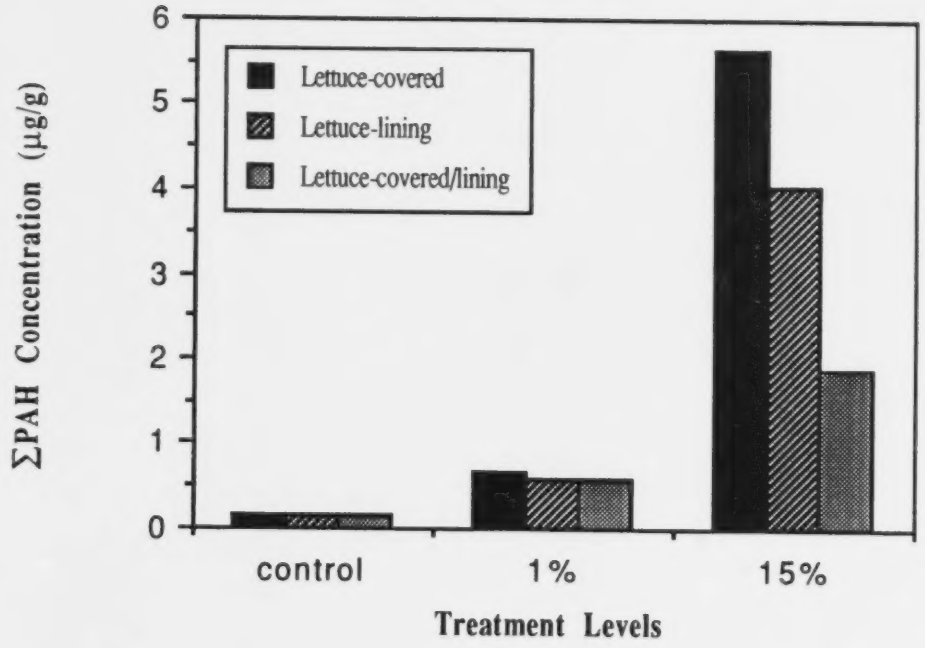


Figure 2.18. Lettuce: Percent Creosote Levels versus Experimental Treatments.

The results of PAH uptake in the lettuce are shown in Table 2.15 and Figure 2.18. Treatment C-RV allowed for a larger PAH uptake into lettuce as compared to C/L-R andL-RA under 15% and 1% treatment levels. There was no growth observed for the 50% and 100% creosote amended treatment levels. The PAH burden with C-RV in 15% and 1% levels were approximately 5.64 µg/g DW and .655 µg/g DW. This translated into a relative uptake of available soil PAH of 0.7% and 2.8% respectively. The relative percent distribution of PAH for each ring class in the lettuce based on the 1% and 15% treatment levels were:

3-ring compounds	21 to 32%
4-ring compounds	57 to 61%
5- and 6-ring compounds	7 to 17%

The differences in the PAH burden in the experiment with treatment C-RV relative to treatments C/L-R and L-RA were due to the 5- and 6-ring compounds. The lettuce samples were washed to remove any type of soil debris and/or dust. However, sorption is stronger with chemicals with higher K_{ow} that bind tightly to the high lipid content lettuce cuticle (Riederer and Schonherr, 1984).

In an overall comparison of barley and lettuce, the lettuce had the highest PAH burden at the 15% treatment level and minimal concentration difference was seen at the 1% level. The structure of the plant and cuticle lipid content can explain some of the differences. Experiments have shown that there is variation in uptake both between species and within the same species on an individual level (Chaney, 1985). Lettuce has broader leaves and growing at ground level allowing a greater surface area for entrapment of the volatile and semi-volatile PAHs. The plant cuticle is not only a route for uptake of organic contaminants, but it may also act as an accumulation compartment for persistent lipophilics.

Extractions of cuticle membranes have shown a large percentage of persistent organic compounds to be in this small fraction of the plant (Riederer, 1990). The barley plant showed lower level of uptake which may be due to the plant height, that allows a greater separation between leaves and the soil surface. Furthermore, barley has a fibrous root network that is not structured to transport large molecules. The lettuce has a well developed root tap that may act, like in the carrot with a well defined lateral stream channels (Topp et al., 1986).

It is important to distinguish between sorption to root surfaces which will be enhanced by high K_{ow} and the likelihood of uptake into the root system and subsequent movement within the plant (Table 2.16). Work by Briggs *et al* (1982) indicates that translocation is greater for compounds of lower K_{ow} because translocation occurs by means of an aqueous carrier fluid. Residence time in the soil is another important consideration. PAHs which are rapidly lost from the soil will be less significant for this pathway (Ryan et al., 1988).

Figure 2.19 and 2.20 show the PAH concentrations detected in carrot peel and cores grown in the control and the creosote amended levels.

Table 2.16 Potential for Uptake based on log K_{ow} and PAH Ring Class

Potential for Root Uptake and Translocation	log Kow	PAH Ring Class
High Potential	<3.5	2-ring
Moderate	<4.5	3-ring
Low	>4.5	4-and 5-ring

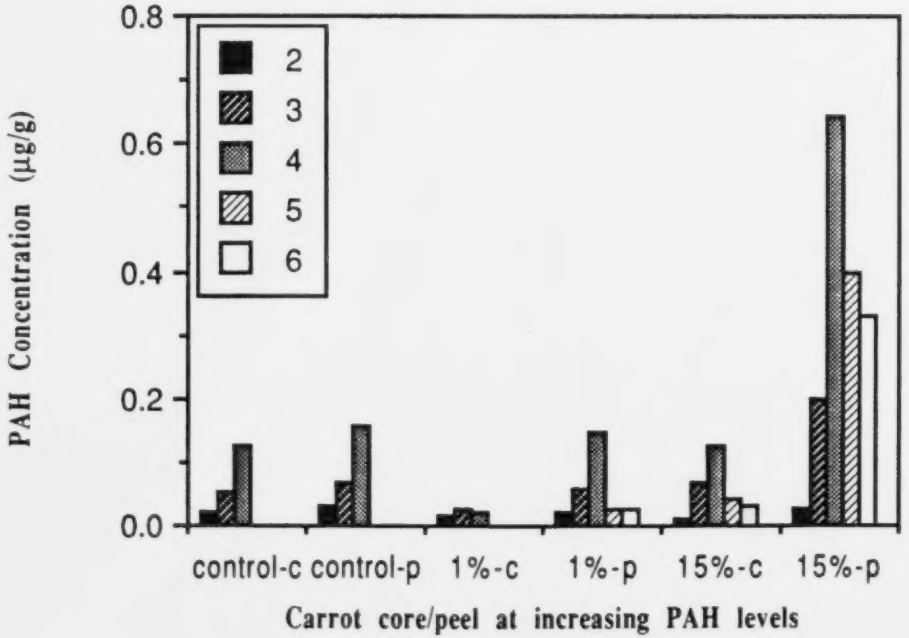


Figure 2.19. Distribution of PAHs by Ring Number for the Carrot Peel and Core at each Creosote Level (Control - 15%).

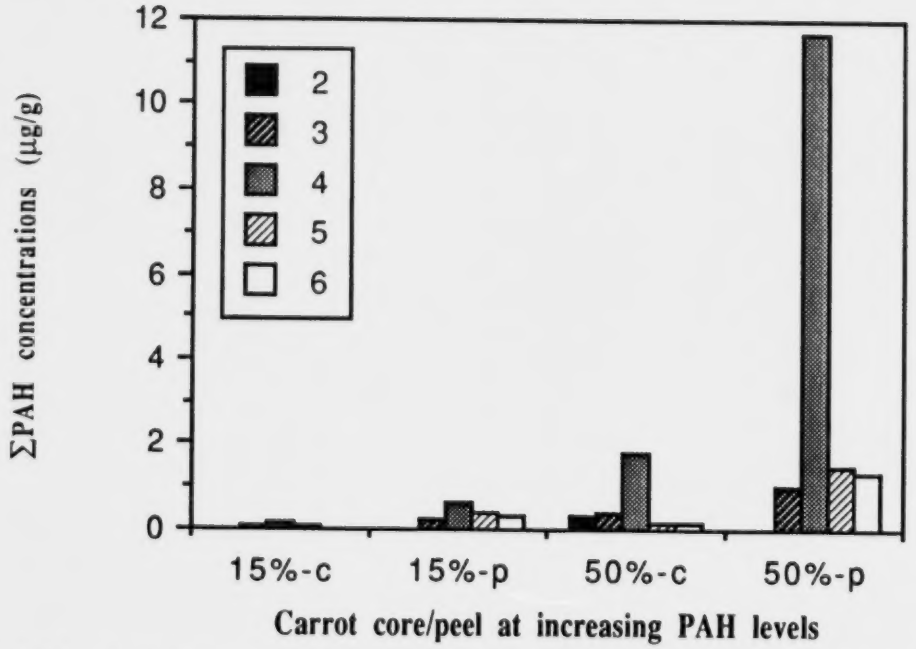


Figure 2.20. Distribution of PAHs by Ring Number for the Carrot Peel and Core at each Creosote Level (15% - 50%).

In both the cores and the peel the PAH burden was dominated by the lower molecular weight compounds, acenaphthene, fluorene and phenanthrene to pyrene (Table 2.17 and 2.18). Dominance of PAH load by low molecular weight compounds in plant tissues has been previously reported (Wild and Jones, 1991b). These molecules are more water soluble than the 5- and 6-ring compounds and may be more susceptible to uptake.

The core PAH concentrations in the carrots were lower than the peel concentrations in all treatment levels (Figure 2.21). The control carrot root peels contained approximately 0.25 µg/g PAH DW. Carrot peels from 15% to 50% creosote amended soils all contained more PAH than the control (Table 2.18). The carrot peels from the 1% creosote level were marginally the same as the control. The peels from the 50% treatment level contained approximately 15.5 µg/g DW. From the epidermal peel to the carrot core there was a substantial decline in the PAH level.

The soil and peel PAH concentrations were not linearly related, however at the lower exposure levels (control -15%) the concentrations in the peel tend to plateau at 600 µg/g. The high concentrations in the 50% creosote level indicate that under such extreme conditions, levels can exceed the plateau reported in other studies (Wild and Jones, 1991b and 1992c).

In general, the peel was found to constitute 40 to 50% of the total carrot weight because of the small size of the carrots (Figure 2.15), and it contained between 70 to 85% of the total carrot PAH burden. Transfer of PAHs from the soil or soil solution to the carrot root appears to be restricted to the peel with little movement into the carrot core. The higher concentrations in the peel were not due to contaminated soil adhesion because the root samples were meticulously cleaned. This result demonstrates the sorption of PAHs

Table 2.17 Carrot Core PAH Concentrations at all Creosote Treatment Levels (µg PAH/ g dry plant matter)

Sample Identification	50% S2 Carrot Core	50% S5 Carrot Core	50% S8 Carrot Core	Standard Deviation {SD}	15% S2 Carrot Core	15% S5 Carrot Core	15% S8 Carrot Core	Standard Deviation {SD}
2-ring								
naphthalene	0.035	0.032	0.056	{0.017}	0.011	0.010	0.011	{0.0006}
3-ring								
acenaphthylene	0.010	0.005	0.005	{0.003}	0.003	0.001	0.001	{0.001}
acenaphthene	0.033	0.011	0.005	{0.004}	0.008	0.004	0.004	{0.002}
fluorene	0.035	0.010	0.004	{0.004}	0.006	0.004	0.004	{0.001}
phenanthrene	0.260	0.046	0.026	{0.014}	0.034	0.017	0.018	{0.009}
anthracene	0.080	0.026	0.029	{0.030}	0.016	0.008	0.007	{0.005}
4-ring								
fluoranthene	0.680	0.480	0.160	{0.23}	0.050	0.027	0.020	{0.016}
pyrene	0.900	0.480	0.420	{0.042}	0.054	0.029	0.017	{0.019}
benzo(a)anthracene	0.065	0.022	0.049	{0.022}	0.006	0.004	0.004	{0.001}
chrysene	0.180	0.110	0.290	{0.091}	0.018	0.014	0.012	{0.003}
5-ring								
benzo(b+k)fluoranthene	0.110	0.079	0.210	{0.068}	0.021	0.021	0.018	{0.002}
benzo(a)pyrene	0.054	0.044	0.072	{0.014}	0.015	0.012	0.012	{0.002}
dibenzo(a,h)anthracene	0.015	0.017	0.021	{0.003}	0.006	0.004	0.004	{0.001}
6-ring								
indeno(1,2,3,-cd)pyrene	0.078	0.064	0.052	{0.013}	0.015	0.013	0.013	{0.001}
benzo(ghi)perylene	0.069	0.062	0.056	{0.007}	0.015	0.013	0.012	{0.002}

{SD} = Standard Deviation was based on a triplicate analysis of the composite plant sample. From the three treatments for each percent creosote level, the treatment (*i.e.* lined)that produced the largest {SD} was reported for each section.

Table 2.17 Continued

Sample Identification	1% S2 Carrot Core	1% S5 Carrot Core	1% S8 Carrot Core	Standard Deviation {SD}	Control S2 Carrot Core	Control S5 Carrot Core	Control S8 Carrot Core	Standard Deviation {SD}
2-ring								
naphthalene	0.015	0.008	0.013	{0.004}	0.021	0.021	0.036	{0.009}
3-ring								
acenaphthylene	<0.001	<0.001	<0.001	{0}	<0.001	<0.001	<0.001	{0}
acenaphthene	0.004	0.004	0.005	{0.0006}	0.017	0.009	0.006	{0.004}
fluorene	0.002	0.002	0.002	{0}	0.004	0.002	0.003	{0.001}
phenanthrene	0.016	0.010	0.015	{0.003}	0.026	0.017	0.013	{0.007}
anthracene	0.002	0.002	0.003	{0.0006}	0.005	0.004	0.003	{0.001}
4-ring								
fluoranthene	0.006	0.008	0.011	{0.003}	0.020	0.011	0.008	{0.002}
pyrene	0.007	0.014	0.017	{0.005}	0.093	0.033	0.023	{0.007}
benzo(a)anthracene								
chrysene	0.006	0.005	0.006	{0.0006}	0.014	0.013	0.006	{0.0007}
5-ring								
benzo(b+k)fluoranthene	<0.001	<0.001	<0.001	{0}	<0.001	<0.001	<0.001	{0}
benzo(a)pyrene	<0.001	<0.001	<0.001	{0}	<0.001	<0.001	<0.001	{0}
dibenzo(a,h)anthracene	<0.001	<0.001	<0.001	{0}	<0.001	<0.001	<0.001	{0}
6-ring								
indeno(1,2,3,-cd)pyrene	<0.001	<0.001	<0.001	{0}	<0.001	<0.001	<0.001	{0}
benzo(ghi)perylene	<0.001	<0.001	<0.001	{0}	<0.001	<0.001	<0.001	{0}

{SD} = Standard Deviation was based on a triplicate analysis of the composite plant sample. From the three treatments for each percent creosote level, the treatment (*i.e.* lined)that produced the largest {SD} was reported for each section.

Table 2.18 Carrot Peel PAH Concentrations at 50%, 15%,1% and Control Treatment Levels (µg PAH/ g dry plant matter)

Sample Identification	50% S2 Carrot Peel	50% S5 Carrot Peel	50% S8 Carrot Peel	Standard Deviation (SD)	15% S2 Carrot Peel	15% S5 Carrot Peel	15% S8 Carrot Peel	Standard Deviation (SD)
2-ring								
naphthalene	0.027	0.051	0.100	(0.017)	0.026	0.066	0.033	(0.021)
3-ring								
acenaphthylene	0.021	0.024	0.088	(0.002)	0.007	0.014	0.007	(0.004)
acenaphthene	0.057	0.130	0.063	(0.004)	0.021	0.044	0.013	(0.016)
fluorene	0.100	0.280	0.240	(0.094)	0.020	0.053	0.016	(0.020)
phenanthrene	0.370	0.550	0.240	(0.16)	0.084	0.240	0.081	(0.002)
anthracene	0.460	0.370	1.320	(0.064)	0.066	0.260	0.130	(0.092)
4-ring								
fluoranthene	4.000	5.970	5.850	(1.10)	0.190	0.440	0.180	(0.007)
pyrene	6.120	7.300	4.980	(1.16)	0.270	0.370	0.180	(0.095)
benzo(a)anthracene	0.500	0.440	0.750	(0.16)	0.042	0.023	0.020	(0.012)
chrysene	1.050	1.450	3.770	(0.28)	0.140	0.160	0.170	(0.015)
5-ring								
benzo(b+k)fluoranthene	0.990	0.960	2.490	(0.021)	0.230	0.290	0.250	(0.031)
benzo(a)pyrene	0.420	0.460	0.940	(0.29)	0.140	0.210	0.180	(0.035)
dibenzo(a,h)anthracene	0.074	0.082	0.150	(0.042)	0.030	0.057	0.044	(0.014)
6-ring								
indeno(1,2,3,-cd)pyrene	0.720	0.670	0.730	(0.032)	0.170	0.220	0.200	(0.025)
benzo(ghi)perylene	0.590	0.540	0.610	(0.036)	0.160	0.240	0.200	(0.040)

(SD) = Standard Deviation was based on a triplicate analysis of the composite plant sample. From the three treatments for each percent creosote level, the treatment (*i.e.* lined)that produced the largest (SD) was reported for each section.

Table 2.18 Continued

Sample Identification	1% S2 Carrot Peel	1% S5 Carrot Peel	1% S8 Carrot Peel	Standard Deviation (SD)	Control S2 Carrot Peel	Control S5 Carrot Peel	Control S8 Carrot Peel	Standard Deviation (SD)
2-ring								
naphthalene	0.019	0.027	0.027	(0.005)	0.029	0.026	0.013	(0.002)
3-ring								
acenaphthylene	0.001	0.002	0.002	(0.0006)	<0.001	<0.001	<0.001	(0)
acenaphthene	0.007	0.011	0.008	(0.002)	0.016	0.009	0.005	(0.002)
fluorene	0.007	0.008	0.008	(0.0006)	0.009	0.005	0.004	(0.001)
phenanthrene	0.035	0.037	0.049	(0.008)	0.035	0.021	0.013	(0.008)
anthracene	0.007	0.011	0.015	(0.004)	0.008	0.002	0.002	(0.004)
4-ring								
fluoranthene	0.051	0.062	0.090	(0.020)	0.033	0.022	0.013	(0.008)
pyrene	0.066	0.051	0.070	(0.010)	0.100	0.059	0.009	(0.015)
benzo(a)anthracene	0.008	0.008	0.007	(0.001)				
chrysene	0.022	0.023	0.023	(0.001)	0.023	0.015	0.007	(0.007)
5-ring								
benzo(b+k)fluoranthene	0.017	0.021	0.023	(0.003)	<0.001	<0.001	<0.001	(0)
benzo(a)pyrene	0.009	0.011	0.009	(0.001)	<0.001	<0.001	<0.001	(0)
dibenzo(a,h)anthracene	<0.001	0.012	0.005	(0.005)	<0.001	<0.001	<0.001	(0)
6-ring								
indeno(1,2,3,-cd)pyrene	0.013	0.023	0.011	(0.006)	<0.001	<0.001	<0.001	(0)
benzo(ghi)perylene	0.012	0.024	0.020	(0.007)	<0.001	<0.001	<0.001	(0)

(SD) = Standard Deviation was based on a triplicate analysis of the composite plant sample. From the three treatments for each percent creosote level, the treatment (*i.e.* lined)that produced the largest (SD) was reported for each section.

from the soil onto a high lipid peel which acts as the first interface for the entry of organic (O'Connor, 1990). However, PAHs were detected in both layers of the carrot root. Figure 2.20 and 2.21 showed that some PAHs have a stronger ability to penetrate deep into the root tissues from the carrot surface. If preferential transport of PAHs through carrot root occurred, there would be differences between the peel and core.

In the greenhouse study, a particular pattern of specific PAH uptake for each layer of the carrot root was not observed. This suggests a variety of possible explanations:

i) the pattern of individual PAH compound uptake has no preferential movement,
ii) PAHs may be taken up by the lateral root and transported deep into the carrot root,
iii) PAHs incorporated into leaf tissues by atmospheric deposition may be translocated from the leaf into the root and/or
iv) PAHs may be biosynthesized in the root (Edwards, 1983).

An overall comparison of exposure pathways via vapors from the soil, foliar uptake and root translocation can be seen with Figure 2.22. This figure represents the highest probability of PAH exposure within the study. The highest uptake was shown in the lettuce under treatment C-RV. However, the carrot peel represents the greatest exposure scenario for any type of vegetation based on soil contact. If root uptake was the dominant mechanism the expected result should be to observe highest PAH uptake in the carrot peel. This indicates that even if the lining was not a complete barrier, volatilizaton of PAHs from the soil and uptake by foliage is a major if not the dominant pathway.

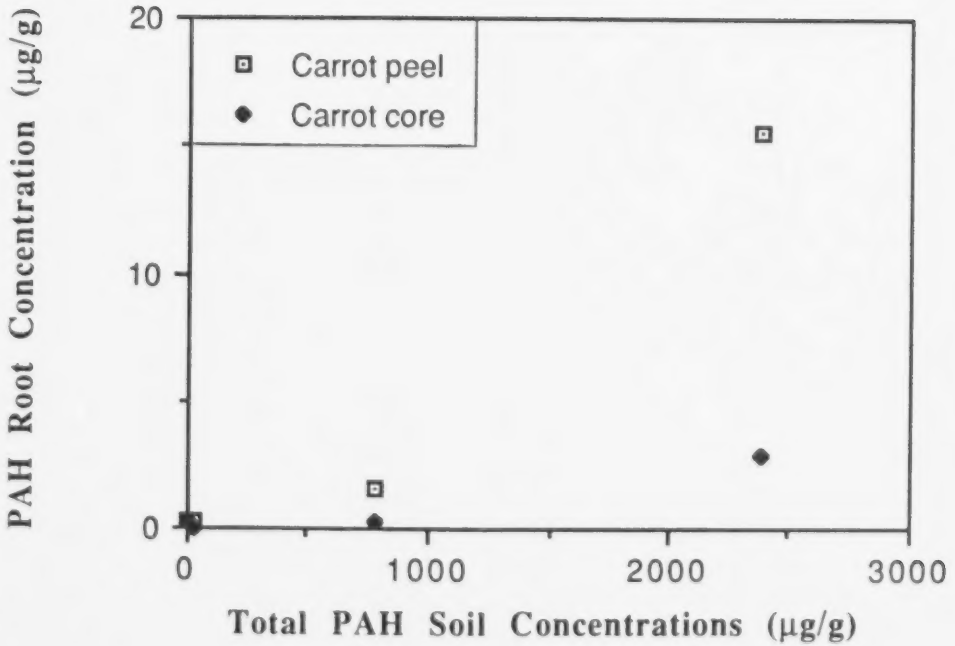


Figure 2.21. Total PAH Concentrations Detected in the Carrot Peels and Cores.

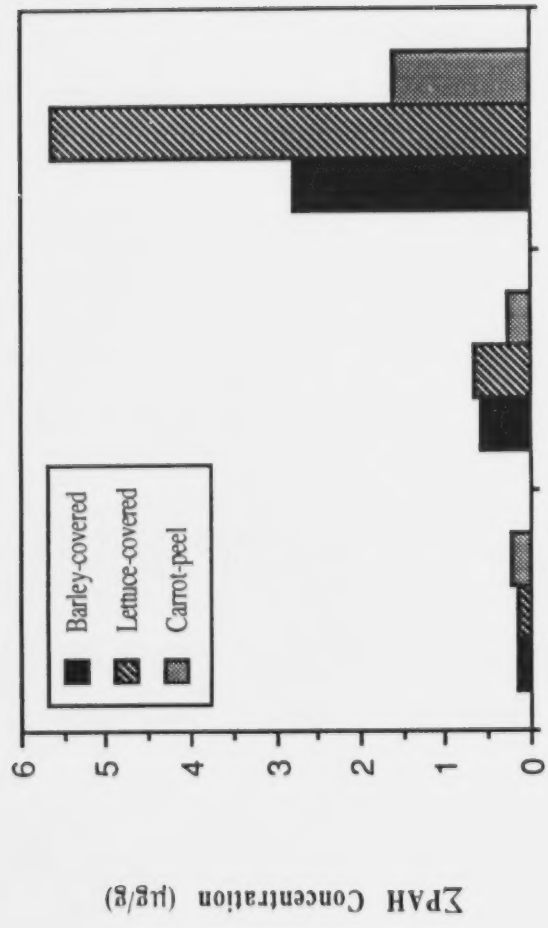


Figure 2.22. Vegetative Uptake from 0-15% Treatment Levels under the Worst Case Scenario for each type of Vegetation Investigated.

The results from the onsite Borradaile experiment did not permit the differentiation of the exposure routes because of the low PAH levels. The preliminary work completed at the site (Pollard and Hrudey, 1992) showed substantially higher PAH concentrations levels than what actually existed. This may have been due to high contamination spots being selected. However, from the data collected, a similar pattern of PAH plant uptake as in the creosote greenhouse experiment was noted.

Results from the two locations on the Borradaile site, site G and D (Figure 2.3) were used for data analysis (Table 2.19 - 2.22). Comparison of barley and lettuce and the corresponding soils from the two sites show that there was a dominant uptake of 3- and 4-ring PAH compounds. The higher molecular weight, 5- and 6-ring compounds had minimal uptake into both types of vegetation (Figure 2.23 and 2.24). Table 2.19 and Figure 2.23 show the control to have higher levels of 3- and 4-ring PAH compounds than the corresponding soil (Table 2.21) which may be explained by air particulate deposition.

Vegetation plays an important role in the determination of the fate and human exposure to organic contaminants in the environment. Exposure pathways to plants as detailed in Chapter 1, include foliar uptake from vapor and aerosol particulate matter and root uptake from soil solution with possible translocation to plant foliage (Paterson *et al.*, 1991a and Topp *et al*, 1986). To assess human exposure by plant ingestion, it is necessary to form a relationship between air, soil and vegetation concentrations.

Correlations described by concentration factors or ratios as presented in Chapter 1 were applied to the data collected in both the greenhouse and Borradaile on-site experiments. Only two correlations were tested with the field data because of the limitation of the appropriate input data collected. The stem concentration factor (equation 6) proposed by Briggs and equation 10 (Chapter 1) relating molecular weight to the plant concentration

factor (Topp *et al*, 1986) were the two relationships examined. The calculated stem concentration factors (SCF) using collected soil and vegetation data (Table 2.23) resulted in low plant uptake factors. The Borradaile input data resulted in higher SCF values for naphthalene and phenanthrene because of the initial low PAH levels in the soil and the chemicals' ability to be taken up within the plant at a faster rate than benzo(a)pyrene, resulting in higher plant/soil ratios. Using the data at hand, the SCF values do not fit the predicted and tested correlation. The explanation of such results may be attributed to the method of data collection for the proposed correlation (Briggs *et al*, 1983). The experiments used nutrient solutions containing the radiolabelled chemicals to observe plant uptake. This type of experiment does not take into account the plant/soil transfer mechanisms nor the behavior of the contaminant in the soil.

Equation 10, relating plant concentration factor to molecular weight did not correlate well with the collected experimental data (Table 2.24). Since the plant/soil ratio or concentration factors were so low, the logarithm of such factors produced negative values, resulting in no direct correlation. The Borradaile on-site data, however, produced a positve CF value only for naphthalene due to the higher level in the plant than in the soil. The root concentration factor (RCF) (equation 1) was attempted for the carrot root peel data, however, because the concentration factors were below the constant 0.82, the logarithm of a negative value was not possible.

Table 2.19 Borradaile - Lettuce, Carrot and Barley at the Garden Site (Site G) (μg PAH/g of dry plant matter)

Sample Identification	Control lining	Background lining	Site G open	Site G covered	Site G covered/ lining	Site G lining	Standard Deviation {SD}
	Lettuce	Lettuce	Lettuce	Lettuce	Lettuce	Carrot	
2-ring							
naphthalene	0.012	0.032	0.028	0.022	0.032	0.024	{0.005}
3-ring							
acenaphthylene	<0.001	0.002	0.004	0.001	<0.001	<0.001	{0.002}
acenaphthene	0.003	0.002	0.014	0.008	0.005	0.005	{0.001}
fluorene	0.005	0.007	0.010	0.004	0.003	0.003	{0.003}
phenanthrene	0.050	0.029	0.018	0.030	0.016	0.009	{0}
anthracene	0.006	0.003	0.004	0.002	0.014	0.002	{0.001}
4-ring							
fluoranthene	0.036	0.052	0.033	0.013	0.032	0.003	{0.005}
pyrene	0.200	0.240	0.041	0.032	0.025	0.005	{0.006}
benzo(a)anthracene	0.006	0.007	0.027	0.007	0.006	<0.001	{0.008}
chrysene	0.007	0.008	0.015	0.002	0.010	<0.001	{0.002}
5-ring							
benzo(b+k)fluoranthene	0.004	0.040	0.016	0.032	<0.001	<0.001	{0.004}
benzo(a)pyrene	0.002	0.004	0.002	0.002	<0.001	<0.001	{0}
dibenzo(a,h)anthracene	0.002	0.006	0.002	0.004	<0.001	<0.001	{0.002}
6-ring							
indeno(1,2,3,-cd)pyrene	0.002	0.004	0.004	0.003	<0.001	<0.001	{0.001}
benzo(ghi)perylene	0.002	0.007	0.004	0.003	<0.001	<0.001	{0.001}

{SD} = Standard Deviation was based on a triplicate analysis of the composite plant sample. From the three treatments for each contamination level, the treatment (*i.e.* lined)that produced the largest {SD} was reported for each section.

Table 2.19 Continued

Sample Identification	Site G lining	Site G covered/ lining	Site G covered	Standard Deviation
	Barley	Barley	Barley	{SD}
2-ring				
naphthalene	0.031	0.063	0.035	{0.001}
3-ring				
acenaphthylene	<0.001	0.001	<0.001	{0}
acenaphthene	0.003	0.006	0.004	{0.001}
fluorene	0.003	0.002	<0.001	{0.002}
phenanthrene	0.018	0.017	0.011	{0.002}
anthracene	0.003	0.003	0.002	{0.002}
4-ring				
fluoranthene	0.013	0.007	0.006	{0.003}
pyrene	0.006	0.014	0.004	{0.001}
benzo(a)anthracene	0.004	0.003	<0.001	{0.002}
chrysene	0.006	0.007	<0.001	{0.001}
5-ring				
benzo(b+k)fluoranthene	<0.001	<0.001	<0.001	{0}
benzo(a)pyrene	<0.001	<0.001	<0.001	{0}
dibenzo(a,h)anthracene	<0.001	<0.001	<0.001	{0}
6-ring				
indeno(1,2,3,-cd)pyrene	<0.001	<0.001	<0.001	{0}
benzo(ghi)perylene	<0.001	<0.001	<0.001	{0}

Table 2.20 Borradaile - Lettuce and Barley at the Drainage Channel Site (Site D) (µg PAH/ g of dry plant matter)

Sample Identification	Site D lining	Site D covered/ lining	Site D covered	Standard Deviation	Site D lining	Site D covered/ lining	Site D covered	Standard Deviation
	Lettuce	Lettuce	Lettuce	{SD}	Barley	Barley	Barley	{SD}
2-ring								
naphthalene	0.022	0.016	0.018	{0.001}	0.018	0.020	0.017	{0.006}
3-ring								
acenaphthylene	0.001	<0.001	0.001	{0}	0.003	<0.001	<0.001	{0.001}
acenaphthene	0.001	0.001	0.001	{0.001}	0.004	0.001	0.005	{0.002}
fluorene	0.003	0.003	0.006	{0.0007}	0.008	0.002	0.002	{0}
phenanthrene	0.014	0.009	0.009	{0.003}	0.018	0.016	0.011	{0.001}
anthracene	0.003	0.001	0.002	{0.005}	0.003	0.004	0.002	{0.001}
4-ring								
fluoranthene	0.005	0.005	0.012	{0.004}	0.017	0.024	0.005	{0.001}
pyrene	0.008	0.004	0.015	{0.007}	0.031	0.058	0.019	{0.006}
benzo(a)anthracene	0.006	0.005	0.003	{0.0007}	0.003	0.004	0.003	{0.001}
chrysene	0.004	0.003	0.005	{0}	0.001	0.005	0.001	{0.004}
5-ring								
benzo(b+k)fluoranthene	0.001	0.002	0.004	{0.0007}	0.030	0.008	0.003	{0.004}
benzo(a)pyrene	0.003	0.002	0.002	{0.0007}	0.002	0.002	0.003	{0.002}
dibenzo(a,h)anthracene	0.007	0.003	0.002	{0.002}	0.005	0.006	0.002	{0.005}
6-ring								
indeno(1,2,3,-cd)pyrene	0.004	0.003	0.003	{0.001}	0.003	0.005	0.002	{0.001}
benzo(ghi)perylene	0.005	0.002	0.003	{0.001}	0.005	0.008	0.002	{0.001}

{SD} = Standard Deviation was based on a triplicate analysis of the composite plant sample. From the three treatments for each contamination level, the treatment (*i.e.* lined)that produced the largest {SD} was reported for each section.

Table 2.21 Borradaile - PAH Soil Concentrations Corresponding to Site G Lettuce, Carrot and Barley Vegetation (μg PAH/g dry wt. basis)

Sample Identification	Control lining	Background lining	Site G open	Site G covered	Site G covered/ lining	Site G lining	Standard Deviation {SD}
	Lettuce	Lettuce	Lettuce	Lettuce	Lettuce	Carrot	
2-ring							
naphthalene	0.007	0.010	0.016	0.021	0.027	0.012	{0.003}
3-ring							
acenaphthylene	0.001	0.001	0.002	0.002	0.002	0.002	{0}
acenaphthene	0.002	0.004	0.004	0.007	0.006	0.004	{0.002}
fluorene	0.002	0.004	0.006	0.005	0.007	0.007	{0.001}
phenanthrene	0.009	0.015	0.027	0.026	0.021	0.018	{0.001}
anthracene	0.001	0.002	0.007	0.006	0.015	0.012	{0.001}
4-ring							
fluoranthene	0.003	0.008	0.021	0.015	0.020	0.015	{0.004}
pyrene	0.003	0.005	0.021	0.014	0.019	0.016	{0.004}
benzo(a)anthracene	0.002	0.003	0.013	0.010	0.012	0.010	{0.002}
chrysene	0.003	0.006	0.033	0.030	0.019	0.019	{0.002}
5-ring							
benzo(b+k)fluoranthene	0.002	0.006	0.017	0.021	0.009	0.009	{0.001}
benzo(a)pyrene	0.001	0.002	0.016	0.011	0.010	0.009	{0.003}
dibenzo(a,h)anthracene	0.008	0.002	0.011	0.006	0.003	0.002	{0.002}
6-ring							
indeno(1,2,3,-cd)pyrene	0.001	0.003	0.025	0.017	0.012	0.008	{0.005}
benzo(ghi)perylene	0.002	0.003	0.029	0.022	0.015	0.010	{0.005}

{SD} = Standard Deviation was based on a triplicate analysis of the composite plant sample. From the three treatments for each contamination level, the treatment (*i.e.* lined)that produced the largest {SD} was reported for each section.

Table 2.21 Continued- PAH Soil Concentrations (μg PAH/g dry wt soil)

Sample Identification	Site G lining	Site G covered/ lining	Site G covered	Standard Deviation
	Barley	Barley	Barley	{SD}
2-ring				
naphthalene	0.026	0.028	0.030	{0.003}
3-ring				
acenaphthylene	0.002	0.002	0.002	{0}
acenaphthene	0.006	0.007	0.005	{0.002}
fluorene	0.005	0.005	0.003	{0.001}
phenanthrene	0.029	0.025	0.022	{0.004}
anthracene	0.008	0.010	0.007	{0.001}
4-ring				
fluoranthene	0.025	0.020	0.019	{0.001}
pyrene	0.020	0.021	0.017	{0.002}
benzo(a)anthracene	0.010	0.013	0.015	{0.001}
chrysene	0.019	0.020	0.016	{0.001}
5-ring				
benzo(b+k)fluoranthene	0.011	0.007	0.019	{0.002}
benzo(a)pyrene	0.012	0.015	0.013	{0.002}
dibenzo(a,h)anthracene	0.004	0.004	0.007	{0.002}
6-ring				
indeno(1,2,3,-cd)pyrene	0.015	0.017	0.025	{0.002}
benzo(ghi)perylene	0.012	0.013	0.011	{0.001}

Table 2.22 Borradaile- PAH Soil Concentrations Corresponding to Site D Lettuce and Barley Vegetation (µg PAH/ g of dry soil)

Sample Identification	Site D lining	Site D covered/ lining	Site D covered	Standard Deviation	Site D lining	Site D covered/ lining	Site D covered	Standard Deviation
	Lettuce	Lettuce	Lettuce	{SD}	Barley	Barley	Barley	{SD}
2-ring								
naphthalene	0.011	0.014	0.014	{0.001}	0.017	0.015	0.015	{0.002}
3-ring								
acenaphthylene	0.001	0.001	0.001	{0}	0.001	0.002	0.002	{0.001}
acenaphthene	0.003	0.003	0.004	{0}	0.004	0.005	0.004	{0.003}
fluorene	0.004	0.009	0.005	{0.001}	0.007	0.008	0.008	{0.001}
phenanthrene	0.021	0.018	0.020	{0.001}	0.027	0.020	0.021	{0.004}
anthracene	0.003	0.003	0.003	{0.001}	0.008	0.012	0.012	{0.001}
4-ring								
fluoranthene	0.012	0.011	0.011	{0.001}	0.019	0.014	0.013	{0.006}
pyrene	0.011	0.008	0.009	{0}	0.023	0.039	0.040	{0.012}
benzo(a)anthracene	0.007	0.004	0.005	{0.001}				
chrysene	0.027	0.017	0.022	{0.007}	0.082	0.150	0.160	{0.007}
5-ring								
benzo(b+k)fluoranthene	0.019	0.015	0.016	{0.001}	0.035	0.070	0.070	{0.010}
benzo(a)pyrene	0.013	0.010	0.010	{0.002}	0.023	0.049	0.050	{0.007}
dibenzo(a,h)anthracene	0.006	0.005	0.005	{0.001}	0.013	0.024	0.023	{0.001}
6-ring								
indeno(1,2,3,-cd)pyrene	0.019	0.015	0.017	{0.006}	0.049	0.078	0.077	{0.009}
benzo(ghi)perylene	0.024	0.020	0.020	{0.006}	0.050	0.072	0.073	{0.001}

{SD} = Standard Deviation was based on a triplicate analysis of the composite plant sample. From the three treatments for each contamination level, the treatment (*i.e.* lined)that produced the largest {SD} was reported for each section.

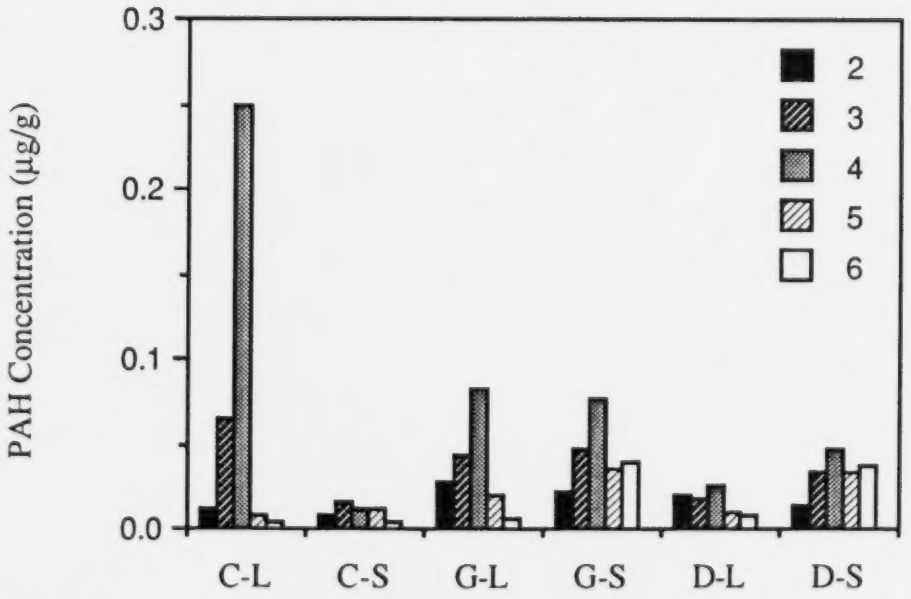


Figure 2.23 Distribution of PAHs by Ring Number for the Control, Garden and Drainage Channel Site Grown Lettuce and Soil.

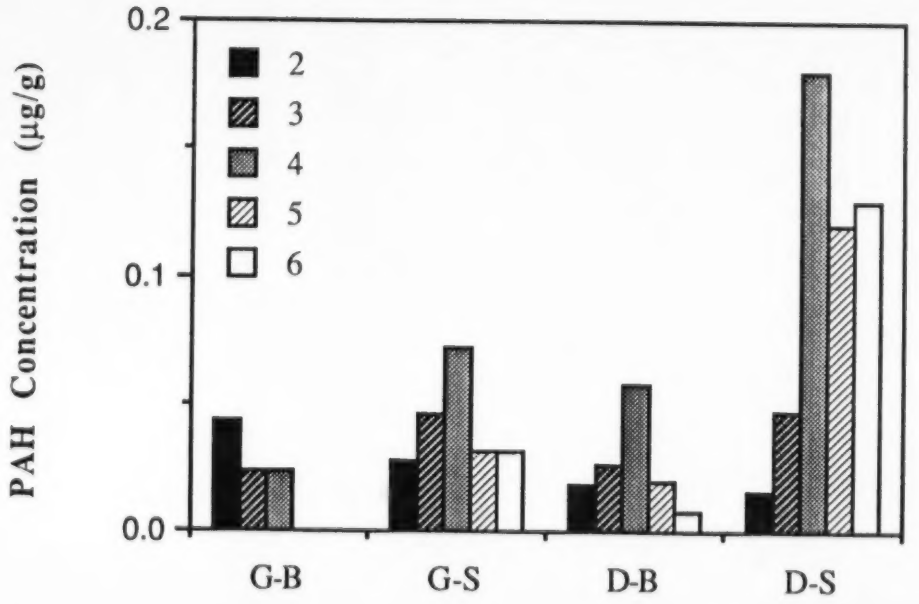


Figure 2.24 Distribution of PAHs by Ring Number for the Garden and Drainage Channel Site Grown Barley and Soil.

Table 2.23 Calculated Stem Concentration Factors (SCF) using Greenhouse and On-site Field Data

PAH	Sample	Measured Stem Concentration Factor (SCF)*	Calculated Stem Concentration Factor (SCF)**
naphthalene	Lettuce - 1%	0.053	4.20
	Lettuce - 15%	0.007	
	Barley - 1%	0.068	
	Barley - 15%	0.003	
	Lettuce - Site G	0.51	
	Barley - Site D	0.46	
phenanthrene	Lettuce - 1%	0.011	0.48
	Lettuce - 15%	0.001	
	Barley - 1%	0.010	
	Barley - 15%	0.0004	
	Lettuce - Site G	0.34	
	Barley - Site D	0.25	
benzo(a)pyrene	Lettuce - 1%	0.009	2.28
	Lettuce - 15%	0.010	
	Barley - 1%	0.004	
	Barley - 15%	0.002	
	Lettuce - Site G	0.07	
	Barley - Site D	0.02	

note: * Stem Concentration Factor (SCF)- plant PAH concentration/soil PAH concentration

** $SCF = [\ 10^{(0.951 \log K_{ow} - 2.05)} + 0.82]\ 0.784 \exp - [\ (\log K_{ow} - 1.78)^2/2.44]$ (Briggs *et al.*, 1982)

Table 2.24 Calculated Plant Concentration Factors using Greenhouse and On-site Field Data

PAH	Sample	Measured Concentration Factor (CF)*	log Measured CF	Calculated log CF**
naphthalene	Lettuce - 1%	0.13	-0.89	0.92
	Lettuce - 15%	0.019	-1.72	
	Barley - 1%	0.17	-0.77	
	Barley - 15%	0.006	-2.22	
	Lettuce - Site G	1.29	0.11	
	Barley - Site D	1.13	0.05	
phenanthrene	Lettuce - 1%	0.027	-1.57	0.58
	Lettuce - 15%	0.003	-2.52	
	Barley - 1%	0.026	-1.59	
	Barley - 15%	0.001	-3.00	
	Lettuce - Site G	0.84	-0.08	
	Barley - Site D	0.65	-0.19	
benzo(a)pyrene	Lettuce - 1%	0.023	-1.64	0.22
	Lettuce - 15%	0.026	-1.59	
	Barley - 1%	0.008	-2.10	
	Barley - 15%	0.006	-2.22	
	Lettuce - Site G	0.17	-0.77	
	Barley - Site D	0.05	-1.30	

note: * Concentration Factor (CF) - plant PAH concentration/soil PAH concentration

** log CF = 5.943 - 2.385 log M (Topp *et al.*, 1986)

Paterson and Mackay (1991) have developed a fugacity based model of a plant which can estimate the concentration of a contaminant in specific plant compartments from air and/or soil contaminant concentrations. In this study, the simplest form of the fugacity model describes a Level I or equilibrium partitioning of organic chemicals in "multi-compartment" plants was used. The plant model is comprised of two bulk compartments, air and soil and the plant which consisits of three compartments, roots, stem and foliage. The air compartment is split into two subcompartments of pure air and aerosol while the soil compartment is divided into air, water, organic and mineral matter. The equations for the fugacity capacities of the various model compartments are listed in Appendix C. The equation expressions are based on physical-chemical properties such as vapor pressure, water solubility, molecular weight and octanol-water partition coefficient (K_{ow}). This model was illustrativelly applied to see the modelled fate of four PAHs: naphthalene, phenanthrene, chrysene and benzo(a)pyrene (Appendix C).

Paterson and Mackay (1991) explained that the level I model is a major simplification of reality. However they state that this method can be used to give order of magnitude concentrations and forms the basis for exposure assessments (Paterson et al., 1991b). Some of the difficulties with such a model are that in the comparmentilization scheme, the root and stem surfaces are not differentiated from the interiors, however the external surfaces have shown to have faster rates of sorption (McFarlane and Wickliff, 1985). Also that equilibrium condtions may never be achieved because of the short life span of a plant, therefore causing the model to be misleading.

The Level I fugacity model was tested by using soil and vegetations concentrations measured in the greenhouse 15% creosote contaminated level. The four PAHs that the model was to be validated for were: napththalene, phenanthrene, chrysene and benzo(a)pyrene. The carrot peel data was used to deal with fugacity model at the root - soil

level. Lettuce and barley was used to test the model with respect to the leaf. The soil concentrations were calculated based on the geometric mean of the initial and final soil PAH concentrations for the greenhouse growth experiment.

The Level I fugacity model assumes equilibrium between the compartments, therefore the fugacities of carrot to soil or lettuce to soil for any of the PAHs should be equal. Table 2.25 shows that the calculated fugacities for the carrots, lettuce and barley do no equal the calculated fugacity for the soil, therefore the basic requirement of equilibrium and steady state conditions by the model were not met. This model will not provide useful absolute predictions for these experiments.

The model predicts that naphthalene and phenanthrene have a greater tendency to be translocated into the leaf compartment than chrysene. In relation to the experimental results, phenanthrene was found to be in the highest abundance in the foliage of barley and lettuce. Chrysene showed high accumulation in the root compartment which is in agreement to its properties of low solubility and high K_{ow}. Benzo(a)pyrene should have shown the same pattern as chrysene but had a higher concentration in the leaf compartment than the root compartment. The fugacities calculated show a decrease with the decrease of the PAH volatility which does correspond to the physico-chemical properties.

There are a number of limitations based on the assumptions and measured values used in this model. The measured plant compartment volumes, densities and approximated water contents are not representative of the variety of plants and their growth environments. Many of the chemicals used for the verification of the model were highly water soluble compounds (i.e. 2,4-D and 1,2,4-TCB) (Paterson *et al.*, 1991b). Also as seen in this experiment, non-equilibrium conditions applied which may be due to the chemical's slow

Table 2.25 Level I Fugacity Based Model Calculations using Soil and Vegetation Concentrations from the 15% Creosote Contaminated Treatment

Physical-Chemical Properties	naphthalene	phenanthrene	chrysene	benzo(a)pyrene
Molecular Weight (g/mol)	128	178	228	252
Solubility (g/m^3)	31.7	1.29	0.002	0.0038
Vapor pressure (Pa)	10.0	0.0161	0.000085	0.0000007
Log K_{ow}	3.37	4.46	5.61	6.04
Z Values (mol/m^3Pa)				
Root	0.66	151.11	34827.01	274457.45
Stem	0.317	70.32	226.45	127434.53
Leaf	1.13	259.92	839.29	472000
Air	0.0004	0.0004	0.0004	0.0004
Water	0.0238	0.45	0.103	21.54
Soil	0.086	19.95	250.54	363120.9
Greenhouse Experiment Concentrations (mol/m^3)				
Carrot root	0.0003	0.0007	0.0006	0.0006
Lettuce leaf	0.0006	0.0019	0.0009	0.0007
Barley leaf	0.0002	0.0008	0.0003	0.0002
Soil	0.046	0.45	0.088	0.037
Fugacity (Pa)* (based on measured concentration)				
Carrot root	0.0004	0.000005	0.00000002	0.000000002
Lettuce leaf	0.0005	0.000007	0.000001	0.000000001
Barley leaf	0.00017	0.0000031	0.00000036	0.0000000004
Soil	0.53	0.023	0.00035	0.000001

note: * If equilibrium had been achieved, fugacities for the different compartments would be equal. Plant concentrations of PAH were much lower than predicted by equilibrium distribution based on fugacity.

uptake, rapid metabolism.or the plants rapid growth.

It should be noted that the points listed are not conceptual limitations of the general modeling method Paterson and Mackay have established Level II and III fugacity models. These models as of yet have not been finalized or validated. Undoubtedly, improvements in structure, parameter values and more specific characteristics for the plant will be found and a series of more reliable, validated models will emerge.

2.3 Conclusions

Plant growth experiments using PAH contaminated soil allowed for the evaluation of the pathways for PAH uptake in selected species of plants. In this study, two types of growth experiments were conducted, a greenhouse and on-site growth experiment. The greenhouse experiment used creosote contaminated soil from a former wood preserving facility, while the on-site growth experiment was performed at a former petroleum processing facility. In both cases, the sites had soil concentration levels of PAHs.

The greenhouse experimental design allowed the investigation of three exposure routes of PAHs to the plants: air particulate deposition, vapor transport from soil to foliage and uptake by root translocation. Similar experiments were carried out at the on-site experiment, however due to low soil PAH levels the exposure pathways to plants could not be differentiated.

The greenhouse growth experiment revealed substantial transfer of PAHs out of the upper soil layer throughout the duration of the experiment. Some of these losses or transfer can be attributed to volatilization which was indicated by air monitoring, while

transfer of PAHs by leaching was indicated by analysis of soils at the bottom of the growth boxes. The 3- and 4-ring PAHs dominated the PAH losses from the soil. The larger 5- and 6-ring PAHs tended to be more resistent to loss due to their large molecular size and low solubility.

The higher levels of creosote in the greenhouse experiment stunted growth for all selected plants. Lettuce and carrots were not able to grow in the 100% creosote level that had total PAH levels exceeding 3500 μg/g. Due to barley's hardiness, it was able to grow at all levels, however, the yields decreased substantially from the control to the 100% creosote growth box.

The highest exposure of PAH levels to barley and lettuce was shown to be under the condition where the plants were covered but were exposed to the soil. This suggests that volatilization of vapors from the soil plays a role in foliar uptake. The levels of PAH were also greater in the lettuce than barley under the same treatment. This was explained as a result of the larger leaf surface area allowing for more efficient entrapment of the volatiles and semi-volatile PAHs. Under the treatment, where the plants were covered but the soil was lined to control volatilization, there was PAH uptake suggesting that root uptake is still important.

The carrot allowed a closer observation of uptake within a root. The PAH concentrations detected in the carrot root peel were all substantially higher than that in the core. This result shows the gradient of PAH in the outer tissue near the contaminated soil compared with the inner core tissue. Approximately 70 to 80% of the PAH burden found in the carrots was associated with the peel.

The Level I fugacity model was tested with the data collected from the greenhouse experiment. This model assumes that the plant/soil system is in equilibrium. Under the growth conditions in the greenhouse, the fugacity model shows that equilibrium was not achieved to allow the use of the equilibrium model. Overall, the models for PAH uptake by plants that were evaluated predicted much higher levels of PAH in plant tissue than were found in the experiment.

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A Risk Assessment Evaluation of Polycyclic Aromatic Hydrocarbon Chronic Dose Exposures at the Borradaile Refinery Site

3.0 Introduction

Human health risk assessment is an important tool for evaluating the potential hazards of human exposure to industrial chemicals, such as petroleum hydrocarbons in air, water and soil. The risk assessment process has evolved over the past twenty years from a qualitative and semi-quantitative approach to one that includes defined methodologies for the quantitative evaluation of hazards posed by exposure to some toxic chemicals, for which the dose response relationship has been estimated.

The goal of any risk assessment is to estimate the probability of an adverse effect on humans, wildlife and/or ecological systems from exposure to a chemical or physical agent. Risk assessment generally consists of four components (Cohrssen and Covello, 1989):

- Source/release assessment: quantitatively estimate the amounts, frequencies, probabilities and locations of the release, or escape of risk agents from specific sources into environment. Four types of quantitative procedures can be used to assess the source and release (Cohrssen and Covello, 1989):

    - Monitoring
    - Accident investigation and performance testing
    - Statistical methods
    - Modeling

- Exposure Assessment: typically estimates the magnitude, duration, schedule and the route of exposure, the populations or ecosystems exposed

to the risk agent, and the uncertainties in all estimates (Davis and Gusman, 1982). This step predicts the concentration of the risk agent that may be absorbed by an individual from various media (water, air, soil and food) following exposure. Exposure is dependent upon the concentration of a chemical in a particular medium and the particular point of contact with the individual. Although direct measurements are preferable, gathering the necessary data to account for such time-activity patterns is difficult and costly. Consequently, contaminant levels are often estimated through modeling. With this information and knowledge of the source, modeling equations can be used to estimate the emission rate, transport and degrees of exposure to a contaminant.

- Dose-Response Assessment: estimating the relationship between different doses and the magnitude of their adverse affects. Dose-response assessment usually entails an extrapolation from the effects resulting from high doses of the risk agent (ie. epidemiologic studies or experimental animal studies) to the lower exposure doses expected from human contact with the agent in the environment. Extrapolation is carried by selecting an extrapolation model that attempts to describe the observed data and then to extend the model from the observed range to the risk expected at low exposure (Cohrssen and Covello, 1989). Uncertainties arise from interspecies extrapolation because of differences in size, metabolism, anatomy, physiology and population heterogeneity.

- Risk characterization: is the last step of the risk assessment process. It is designed to generate several types of estimates from the results of

source/release, exposure, and the dose-response assessments (Cohrssen and Covello, 1989). These estimates are accompanied by a description and discussion of uncertainties and analytical assumptions, because characterizing risk includes characterizing uncertainty and underlying assumptions.

The National Research Council (1983) has identified some of the key questions that serve as decision points facing the risk analyst in this final step (Cohrssen and Covello, 1989):

- "What are the statistical uncertainties in estimating the extent of health effect? How are these uncertainties to be computed and presented?

- What are the biological uncertainties in estimating the extent of health effects? What is the origin? How will they be estimated? What effect do they have on quantitative estimates? How will the uncertainties be described to decison makers?

- Which dose-response assessments and exposure assessment scenarios should be used?

- Which population groups should be the primary targets for protection, and which provide the most meaningful expression of the health risks?"

The steps of hazard identification and dose-response assessment have been the subject of considerable controversy. Debate in these areas, although impacting the science of risk assessment, is largely confined to the regulatory policy-making assessor.

The primary area where the individual risk assessor can and does have a major impact is the exposure assessment step. This step is where the assessor combines site characterization into the assessment and estimates potential risks associated with a given contaminant. Careful selection of exposure assumptions is critical to generate reliable estimates of chemical uptake and the prediction of associated health risks. The critical factors that should be considered in an exposure assessment include (Paustenbach, 1989):

- appropriate data analysis, including quality assurance and control;
- qualitative and quantitative estimation of transport and distribution of contaminants in the media of interest;
- identification of all pertinent exposure routes and potentially exposed populations or ecosystems;
- accurate estimation of exposure parameters such as:
  - medium ingestion rates,
  - dermal contact rates,
  - inhalation rates, and
  - bioavailability of chemicals following exposure.

In this work, the objective of the Borradaile Risk Assessment was to identify significant petroleum contaminants, particularly polycyclic aromatic hydrocarbons (PAHs), and the exposure pathways which may contribute to the health risk of receptors who may be exposed. These hydrocarbons are the products of combustion and pyrolysis and are present in petroleum and coal and products derived from them. Most PAHs are not carcinogenic, however a few are strong inducers of skin and lung tumors in mice. The most effective carcinogens among PAHs are the 5- and 6-ring compounds. These PAHs tend to be less prevalent in creosote and/or oil mixtures than the 3- and 4-ring PAHs, most

of which are not carcinogenic. This assessment used data generated from Phase I and II of this study to investigate the exposure to four PAHs. The parameters considered included site characterization and a vague method to select chemical indicators (PAHs) and their concentrations.

In the original health risk assessment for the site (Concord, 1991), the lack of direct exposure data was compensated by using models to trace contaminant movement and partitioning were used to estimate the concentrations within certain media (air, water, soil and dust). The models were also used to estimate the exposure estimates which might affect the receptors on-site by exposure pathways such as ingestion, inhalation and dermal contact. The pathways analysis and risk estimation generally followed procedures recommended by the U.S. Environmental Protection Agency (U.S. EPA, 1986, 1988, 1989).

The original risk asssessment by Concord dealt specifically with suspended particulates as the only exposure pathway for inhalation of PAHs. The chronic exposure from the inhalation of suspended particulates was assumed to be the same as the chronic exposure due to ingestion of suspended particulates (Concord, 1991). The contribution of the vapor phase of PAHs to the inhalation exposure was not addressed (Concord, 1991). The greenhouse growth experiment which was performed to study PAH exposure to plants used fresh creosote that resulted in atmospheric levels of naphthalene, phenanthrene and pyrene. Benzo(a)pyrene vapor levels were at the analytical detection limit of 1 part per billion (ppb). Of the four indicator PAHs, the vapors that are of concern in a final risk assessment are benzo(a)pyrene due to its potential carcinogenicity. Measured benzo(a)pyrene levels (6.18 $\mu g/m^3$ to non-detection within a 5 week period) resulted in substantial increase (2.0 $\mu g/kg/d$ for the adult receptor) of the overall inhalation exposure. It must be noted that the reported vapor levels were from the greenhouse experiment using

a fresh source of PAHs under confined conditions. However, this study will not explicitly address volatile exposures to keep in accordance with the original Concord assessment. Likewise, this study will focus on the relative exposures of PAHs *via* transmission of soil and vegetation, the primary routes identified by Concord for the overall evaluation of the original assessment.

Within the assessment that was performed at the Borradaile Site, the adult receptor was a maximally exposed person to a simulated exposure pattern of contaminants at the site. The purpose of an assessment is to cautiously estimate the activities (err on the side of caution) of the exposed receptor and to acknowledge the key assumptions which correspond to each activity. The assessment assumes the receptor to live on the site for an approximate 70 years, participating in the detailed activities resulting in the exposure to the contaminants (Concord, 1991).

The Borradaile risk assessment used an adult and a child as the receptors for assessing the health risk. Because the re-evaluation of the original risk assessment is based only upon using different inputs for soil and vegetation PAH levels, only the calculations for the adult receptor are re-evaluated to determine the relative importance of using measured field data.

The process of estimating the dose received by individuals during their exposure to on-site contaminants at hazardous waste sites requires many assumptions, inferences and simplifications. While the appropriate use of conservative assumptions during risk assessment is generally prudent, the compounding effect of several worst case exposure scenarios is often to render the resultant risk estimate unreasonable to the point where

inappropriate risk management options may be proposed or reasonable options excluded. This re-evaluation of some major unconfirmed exposure assumptions sought to provide a more representative estimate of actual site exposures to PAHs.

The PAH contributions from the various pathways have been calculated using the same approach proposed by Concord (1991) to estimate the dose delivered to the specific receptors (Appendix D). Because of the lack of data collected for the interpretation of this particular risk assessment, a very conservative approach was originally used by Concord (1991), involving two dose estimate ranges- base case and lower estimate case. Oil and Grease (O&G) values measured at the site with the probable range of the various groups of PAH presented as fractions of O&G were used. The highest O&G value was taken as the base case or the worst case scenario. For sensitivity testing, the original risk assessment also used a lower case estimate of the dose based on the lowest O&G concentration in the soil (Concord, 1991).

In this experimental project, field data for the soil and vegetation were collected at the most probable exposure sites (*e.g.* garden site and drainage site) at Borradaile to obtain a more realistic exposure scenario. Exposure estimates were calculated from the field data using the same dose estimate models as the risk assessment. The exposures calculated with field data were designated as the field case. This paper will compare the field case exposure doses to the Concord (1991) risk assessment's estimated base and lower estimate cases.

The Borradaile site is located in Alberta, 10 km east of Vermillion on Highway 16 and is now controlled by Forestry, Lands and Wildlife together with a private owner, the Brokops. The heavy crude wastes on the site are the result of the operations of Borradaile

Oils Ltd. and Husky Oil Operations. The land was used to facilitate crude treatment with processes such as skimming (oil and water separation), desalting, and crude transfer to rail cars with rail tracks extending into the property beside the drainage channel. The damaged areas includes a drainage channel which still vents off hydrocarbons, two former disposal pits which were used to discard excess crude, and the garden area which was the original location of the process plant. The only decommissioning activities that were carried out were removing large equipment to Lloydminster and backfilling the disposal pits to within 0.5 m of the ground surface.

3.1 Methods and Materials

Details of experimental design, setup and analytical methods used for the Borradaile Site experiment were previously described in Chapter 2 section 2.1.

3.2 Results and Discussion

Risk assessment for PAHs requires quantitative estimates of the intensity and sources of exposure to individuals or general populations (Ruttenber, 1993). There is a need to define the exposures associated with multimedia pathways for PAHs as individual components and as a group (Krewski *et al.*, 1989). A combination of site monitoring data and environmental modeling results are used to estimate exposure pathways. Because site monitoring data alone will not reveal the pollutant movement, environmental fate modeling is used by the EPA. The original Borradaile risk assessment (Concord, 1991) followed a formalized assessment procedure which has been developed by the U.S. EPA and was largely adopted for this case.

The first basic step of a risk assessment was the selection of indicator chemicals. Some of the principal guidelines and methods that were used in the selection of compounds used to assess the public health risk include (Concord, 1991):

- selection of compounds from each of the major classes of chemical compounds to which receptors are likely to be exposed;
- examination of the USEPA delisting manual which included guidance on the constituents of petroleum wastes;
- analysis of recorded analytical data that existed for the various HELP sites at levels that are likely to be of concerns; and
- chemical analysis of the composition of the source medium.

The selection for specific PAHs was based upon historical background check of the site to develop a list of probable compounds expected at the site and their toxicity, mobility, persistence and concentration (Concord, 1991). Naphthalene, phenanthrene, chrysene and benzo(a)pyrene were chosen as the indicator chemicals for the health risk assessment. These four compounds represent the range of physical-chemical properties and health considerations present in the PAHs and include a 2-, 3-, 4- and 5-ring PAH. They cover the range of medium to low solubility and volatility and medium to very slow rates of degradation. There is a relatively high level of toxicity concern for benzo(a)pyrene, medium for chrysene, and low toxicity for naphthalene and phenanthrene. Benzo(a)pyrene was chosen because of its probable carcinogenicity.

Benzo(a)pyrene is often taken as the indicator for 5- and 6-ringed PAH compounds which are the probable carcinogenic members of this family of compounds. Although, benzo(a)pyrene was not detected at the site from data collected during earlier site assessments (Concord, 1991), actual soil and vegetation field data (Table 3.1 to 3.4) collected for the uptake experiments did find detectable levels of benzo(a)pyrene and the other 2- to 4-ring PAH compounds.

Previous work dealing with PAHs, have used benzo(a)pyrene as a single representative surrogate for all 16 members (Osborne and Crosby, 1987). Because of the varying physico-chemical and biological properties of an individual PAH, estimating exposure to this specific compound does not represent the environmental status of the other common PAHs. Table 3.1 and 3.2 show that the concentration ratio between naphthalene and benzo(a)pyrene is 10:1 indicating the benzo(a)pyrene surrogate is not representative of the amount of other PAHs present.

Table 3.1 Borradaile - Lettuce, Carrot and Barley at the Garden Site (Site G) (μg PAH/g of dry plant matter)

Sample Identification	Control lining	Background lining	Site G open	Site G covered	Site G covered/ lining	Site G lining	Standard Deviation {SD}
	Lettuce	Lettuce	Lettuce	Lettuce	Lettuce	Carrot	
2-ring							
naphthalene	0.012	0.032	0.028	0.022	0.032	0.024	{0.005}
3-ring							
acenaphthylene	<0.001	0.002	0.004	0.001	<0.001	<0.001	{0.002}
acenaphthene	0.003	0.002	0.014	0.008	0.005	0.005	{0.001}
fluorene	0.005	0.007	0.010	0.004	0.003	0.003	{0.003}
phenanthrene	0.050	0.029	0.018	0.030	0.016	0.009	{0}
anthracene	0.006	0.003	0.004	0.002	0.014	0.002	{0.001}
4-ring							
fluoranthene	0.036	0.052	0.033	0.013	0.032	0.003	{0.005}
pyrene	0.200	0.240	0.041	0.032	0.025	0.005	{0.006}
benzo(a)anthracene	0.006	0.007	0.027	0.007	0.006	<0.001	{0.008}
chrysene	0.007	0.008	0.015	0.002	0.010	<0.001	{0.002}
5-ring							
benzo(b+k)fluoranthene	0.004	0.040	0.016	0.032	<0.001	<0.001	{0.004}
benzo(a)pyrene	0.002	0.004	0.002	0.002	<0.001	<0.001	{0}
dibenzo(a,h)anthracene	0.002	0.006	0.002	0.004	<0.001	<0.001	{0.002}
6-ring							
indeno(1,2,3,-cd)pyrene	0.002	0.004	0.004	0.003	<0.001	<0.001	{0.001}
benzo(ghi)perylene	0.002	0.007	0.004	0.003	<0.001	<0.001	{0.001}

{SD} = Standard Deviation was based on a triplicate analysis of the composite plant sample. From the three treatments for each contamination level, the treatment (*i.e.* lined)that produced the largest {SD} was reported for each section.

Table 3.1 Continued

Sample Identification	Site G lining	Site G covered/ lining	Site G covered	Standard Deviation
	Barley	Barley	Barley	{SD}
2-ring				
naphthalene	0.031	0.063	0.035	{0.001}
3-ring				
acenaphthylene	<0.001	0.001	<0.001	{0}
acenaphthene	0.003	0.006	0.004	{0.001}
fluorene	0.003	0.002	<0.001	{0.002}
phenanthrene	0.018	0.017	0.011	{0.002}
anthracene	0.003	0.003	0.002	{0.002}
4-ring				
fluoranthene	0.013	0.007	0.006	{0.003}
pyrene	0.006	0.014	0.004	{0.001}
benzo(a)anthracene	0.004	0.003	<0.001	{0.002}
chrysene	0.006	0.007	<0.001	{0.001}
5-ring				
benzo(b+k)fluoranthene	<0.001	<0.001	<0.001	{0}
benzo(a)pyrene	<0.001	<0.001	<0.001	{0}
dibenzo(a,h)anthracene	<0.001	<0.001	<0.001	{0}
6-ring				
indeno(1,2,3,-cd)pyrene	<0.001	<0.001	<0.001	{0}
benzo(ghi)perylene	<0.001	<0.001	<0.001	{0}

Table 3.2 Borradaile - Lettuce and Barley at the Drainage Channel Site (Site D) (μg PAH/ g of dry plant matter)

Sample Identification	Site D lining	Site D covered/ lining	Site D covered	Standard Deviation	Site D lining	Site D covered/ lining	Site D covered	Standard Deviation
	Lettuce	Lettuce	Lettuce	{SD}	Barley	Barley	Barley	{SD}
2-ring								
naphthalene	0.022	0.016	0.018	{0.001}	0.018	0.020	0.017	{0.006}
3-ring								
acenaphthylene	0.001	<0.001	0.001	{0}	0.003	<0.001	<0.001	{0.001}
acenaphthene	0.001	0.001	0.001	{0.001}	0.004	0.001	0.005	{0.002}
fluorene	0.003	0.003	0.006	{0.0007}	0.008	0.002	0.002	{0}
phenanthrene	0.014	0.009	0.009	{0.003}	0.018	0.016	0.011	{0.001}
anthracene	0.003	0.001	0.002	{0.005}	0.003	0.004	0.002	{0.001}
4-ring								
fluoranthene	0.005	0.005	0.012	{0.004}	0.017	0.024	0.005	{0.001}
pyrene	0.008	0.004	0.015	{0.007}	0.031	0.058	0.019	{0.006}
benzo(a)anthracene	0.006	0.005	0.003	{0.0007}	0.003	0.004	0.003	{0.001}
chrysene	0.004	0.003	0.005	{0}	0.001	0.005	0.001	{0.004}
5-ring								
benzo(b+k)fluoranthene	0.001	0.002	0.004	{0.0007}	0.030	0.008	0.003	{0.004}
benzo(a)pyrene	0.003	0.002	0.002	{0.0007}	0.002	0.002	0.003	{0.002}
dibenzo(a,h)anthracene	0.007	0.003	0.002	{0.002}	0.005	0.006	0.002	{0.005}
6-ring								
indeno(1,2,3,-cd)pyrene	0.004	0.003	0.003	{0.001}	0.003	0.005	0.002	{0.001}
benzo(ghi)perylene	0.005	0.002	0.003	{0.001}	0.005	0.008	0.002	{0.001}

{SD} = Standard Deviation was based on a triplicate analysis of the composite plant sample. From the three treatments for each contamination level, the treatment (*i.e.* lined)that produced the largest {SD} was reported for each section.

Table 3.3 Borradaile - PAH Soil Concentrations Corresponding to Site G Lettuce, Carrot and Barley Vegetation (µg PAH/g dry wt. basis)

Sample Identification	Control lining	Background lining	Site G open	Site G covered	Site G covered/ lining	Site G lining	Standard Deviation {SD}
	Lettuce	Lettuce	Lettuce	Lettuce	Lettuce	Carrot	
2-ring							
naphthalene	0.007	0.010	0.016	0.021	0.027	0.012	{0.003}
3-ring							
acenaphthylene	0.001	0.001	0.002	0.002	0.002	0.002	{0}
acenaphthene	0.002	0.004	0.004	0.007	0.006	0.004	{0.002}
fluorene	0.002	0.004	0.006	0.005	0.007	0.007	{0.001}
phenanthrene	0.009	0.015	0.027	0.026	0.021	0.018	{0.001}
anthracene	0.001	0.002	0.007	0.006	0.015	0.012	{0.001}
4-ring							
fluoranthene	0.003	0.008	0.021	0.015	0.020	0.015	{0.004}
pyrene	0.003	0.005	0.021	0.014	0.019	0.016	{0.004}
benzo(a)anthracene	0.002	0.003	0.013	0.010	0.012	0.010	{0.002}
chrysene	0.003	0.006	0.033	0.030	0.019	0.019	{0.002}
5-ring							
benzo(b+k)fluoranthene	0.002	0.006	0.017	0.021	0.009	0.009	{0.001}
benzo(a)pyrene	0.001	0.002	0.016	0.011	0.010	0.009	{0.003}
dibenzo(a,h)anthracene	0.008	0.002	0.011	0.006	0.003	0.002	{0.002}
6-ring							
indeno(1,2,3,-cd)pyrene	0.001	0.003	0.025	0.017	0.012	0.008	{0.005}
benzo(ghi)perylene	0.002	0.003	0.029	0.022	0.015	0.010	{0.005}

{SD} = Standard Deviation was based on a triplicate analysis of the composite plant sample. From the three treatments for each contamination level, the treatment (*i.e.* lined)that produced the largest {SD} was reported for each section.

Table 3.3 Continued- PAH Soil Concentrations (μg PAH/g dry wt soil)

Sample Identification	Site G lining	Site G covered/ lining	Site G covered	Standard Deviation
	Barley	Barley	Barley	(SD)
2-ring				
naphthalene	0.026	0.028	0.030	(0.003)
3-ring				
acenaphthylene	0.002	0.002	0.002	(0)
acenaphthene	0.006	0.007	0.005	(0.002)
fluorene	0.005	0.005	0.003	(0.001)
phenanthrene	0.029	0.025	0.022	(0.004)
anthracene	0.008	0.010	0.007	(0.001)
4-ring				
fluoranthene	0.025	0.020	0.019	(0.001)
pyrene	0.020	0.021	0.017	(0.002)
benzo(a)anthracene	0.010	0.013	0.015	(0.001)
chrysene	0.019	0.020	0.016	(0.001)
5-ring				
benzo(b+k)fluoranthene	0.011	0.007	0.019	(0.002)
benzo(a)pyrene	0.012	0.015	0.013	(0.002)
dibenzo(a,h)anthracene	0.004	0.004	0.007	(0.002)
6-ring				
indeno(1,2,3,-cd)pyrene	0.015	0.017	0.025	(0.002)
benzo(ghi)perylene	0.012	0.013	0.011	(0.001)

Table 3.4 Borradaile- PAH Soil Concentrations Corresponding to Site D Lettuce and Barley Vegetation (μg PAH/ g of dry soil)

Sample Identification	Site D lining	Site D covered/ lining	Site D covered	Standard Deviation	Site D lining	Site D covered/ lining	Site D covered	Standard Deviation
	Lettuce	Lettuce	Lettuce	{SD}	Barley	Barley	Barley	{SD}
2-ring								
naphthalene	0.011	0.014	0.014	{0.001}	0.017	0.015	0.015	{0.002}
3-ring								
acenaphthylene	0.001	0.001	0.001	{0}	0.001	0.002	0.002	{0.001}
acenaphthene	0.003	0.003	0.004	{0}	0.004	0.005	0.004	{0.003}
fluorene	0.004	0.009	0.005	{0.001}	0.007	0.008	0.008	{0.001}
phenanthrene	0.021	0.018	0.020	{0.001}	0.027	0.020	0.021	{0.004}
anthracene	0.003	0.003	0.003	{0.001}	0.008	0.012	0.012	{0.001}
4-ring								
fluoranthene	0.012	0.011	0.011	{0.001}	0.019	0.014	0.013	{0.006}
pyrene	0.011	0.008	0.009	{0}	0.023	0.039	0.040	{0.012}
benzo(a)anthracene	0.007	0.004	0.005	{0.001}				
chrysene	0.027	0.017	0.022	{0.007}	0.082	0.150	0.160	{0.007}
5-ring								
benzo(b+k)fluoranthene	0.019	0.015	0.016	{0.001}	0.035	0.070	0.070	{0.010}
benzo(a)pyrene	0.013	0.010	0.010	{0.002}	0.023	0.049	0.050	{0.007}
dibenzo(a,h)anthracene	0.006	0.005	0.005	{0.001}	0.013	0.024	0.023	{0.001}
6-ring								
indeno(1,2,3,-cd)pyrene	0.019	0.015	0.017	{0.006}	0.049	0.078	0.077	{0.009}
benzo(ghi)perylene	0.024	0.020	0.020	{0.006}	0.050	0.072	0.073	{0.001}

{SD} = Standard Deviation was based on a triplicate analysis of the composite plant sample. From the three treatments for each contamination level, the treatment (*i.e.* lined)that produced the largest {SD} was reported for each section.

The site assessment available to Concord (1991) had a number of gaps for the purpose of risk assessment, particularly with the organic chemical analysis of the oil and grease fraction (O&G). Only one soil sample was analyzed in detail, including the characterization of the oil fraction. Little information on location and type of sample was reported. Also, no benzo(a)pyrene was detected explicitly in this one soil sample. Because of insufficient direct PAH data from the Borradaile site, the original Borradaile risk assessment estimated PAH concentrations by calculating concentration as a fraction of O&G content. The PAH/O&G ratio for the base and lower estimate case was 1:4000 or converted to a PAH source factor of 250 ppm (250 mg/kg) (Concord, 1991).

Using the original terminology of the Concord (1991) report the "base" estimate case represents the worst case scenario. The highest O&G concentration from the Borradaile Site was converted to a PAH concentration by multiplying the O&G concentration by the PAH/O&G ratio of 250 mg/kg. For the base estimate case, the PAH concentration in the soil was 6.5×10^3 µg/kg (= 26,000 mg O&G/kg x 250 mg PAH/ 10^6 mg O&G). Sensitivity testing was performed using a lower estimate case of the dose (Concord, 1991). The lowest O&G concentration at the Borradaile Site, 32 mg/kg, was multiplied by the PAH source factor of 250 mg PAH/10^6 mg of O&G to give a soil PAH concentration of 8.0×10^{-3} µg/kg. The field estimate case soil PAH concentrations (Table 3.3 and 3.4), were measured from selected locations on the Borradaile site. These sites denoted as: sites B (background), C (control), G (garden) and D (drainage channel) were used to grow vegetation under the experimental design discussed in Chapter 2 to investigate PAH uptake into plants from PAH contaminated soils. The average field case soil PAH concentrations used in the dose estimate models for each of the four indicator PAHs is presented in Table 3.9.

The field estimate case PAH concentrations for vegetation were taken as the average PAH concentration of barley and lettuce grown at the Borradaile Site. The barley and lettuce concentrations were combined, since concentrations did not vary considerably and that the assumed plant in the original risk assessment was a combined leaf and tap root plant. Each of the four PAHs used for the assessment have their own specific value. Table 3.6 shows the measured mean vegetation PAH concentrations collected from the Borradaile on-site experiment. No surrogate PAH was used as in the case of the original Borradaile risk assessment.

Tables 3.5 to 3.9 are the PAH contaminant concentrations that were input into the risk assessment dose estimate models shown in Appendix D. Table 3.5 shows the calculated vegetation PAH concentrations using the plant uptake models used by Concord (Appendix D) for the four selected PAHs using the estimated soil concentrations from Table 3.7.

Table 3.5 Calculated Contaminated Produce Concentrations - Base Estimate Case (See Appendix D1.1.1)

Routes of Plant Upake	Benzo(a)pyrene µg/kg	Phenanthrene µg/kg	Chrysene µg/kg	Naphthalene µg/kg
Foliar deposition	2.8E-01	2.6E-02	2.8E-01	6.8E-03
Root uptake	6.1E+01	3.6E+02	9.6E+01	1.3E+03
TOTAL	6.1E+01	3.6E+02	9.6E+01	1.3E+03

note: data from the Health Risk Assessment Study of Former Borradaile Refinery Site prepared by Concord Environmental Corporation, 1991.

Table 3.6 Measured Mean Contaminant Concentrations in Produce (Average of Barley and Lettuce Grown at the Borradaile Site)- Field Estimate Case

Routes of Plant Uptake	Benzo(a)pyrene µg/kg	Phenanthrene µg/kg	Chrysene µg/kg	Naphthalene µg/kg
TOTAL	2.0E+00	1.7E+01	4.0E+00	2.1E+01

note: the data is the calculated mean of the anlayzed barley and lettuce for each specific PAH (see Table 3.1 and 3.2).

The PAH concentrations used for dust and dust-tilling (Table 3.7 to 3.9) were also based on the PAH source factor. Dust and dust-tilling data was calculated using conversion assumptions based on the original Borradaile risk assessment (Concord, 1991). These PAH source factors were applied to the soil PAH concentrations to obtain the dust and dust-tilling PAH concentrations. For dust values, the ambient concentration of total suspended solids (TSP) was assumed to be 60 $\mu g/m^3$(Concord, 1991). The value was selected because of:

- the value was the National Ambient Air Quality Objective for TSP;
- the value was greater than the calculated results based on the equation for TSP due to wind erosion of open areas; and
- the concentration of fine particulate soil which may remain in the air is unlikely higher than this value.

The ambient PAH air concentration was estimated by multiplying the soil PAH concentration by the ambient concentration of TSP of 60 $\mu g/m^3$.

The ambient PAH air concentration during tillage was estimated by multiplying the ambient concentration of TSP of 0.29 g/m^3 by the soil PAH concentration. The estimation of the ambient concentration of TSP was based on the following equation (Concord, 1991):

$$E = \frac{1234\ s\ S}{(PE)^2}$$

where:

E = emission per tilling (kg/ha)

s = silt content of soil expressed as a percent, 3%

S = average machinery speed, ~2.5 m s^{-1}

PE = Thornwaite's precipitation-evaporation index, 40

The estimated PAH soil concentrations in Tables 3.7 and 3.8 were used by the original Borradaile risk assessment . These estimated soil concentrations were used to calculate concentrations of dust and dust-tilling to be used for the dose estimate models for the base and lower estimate cases. The estimated PAH soil concentrations were derived from a ratio or PAH source factor multiplied by the O&G concentration of the soil to calculate a soil concentration.

Table 3.7 Calculated Contaminant Concentrations for Direct Pathway Exposures of Receptors at the Borradaile Site - Base Estimate Case

Pathway	Units	Benzo(a)pyrene	Phenanthrene	Chrysene	Naphthalene
Soil	µg PAH/kg Soil	6.5E+03	6.5E+03	6.5E+03	6.5E+03
Dust	µg PAH/m^3 Air	3.9E-04	3.9E-04	3.9E-04	3.9E-04
Dust-tilling	µg PAH/m^3 Air	1.9E+00	1.9E+00	1.9E+00	1.9E+00

note: cited from Concord, 1991.

Table 3.8 Calculated Contaminant Concentrations for Direct Exposure Pathways of Receptors at the Borradaile Site - Lower Estimate Case

Pathway	Units	Benzo(a)pyrene	Phenanthrene	Chrysene	Naphthalene
Soil	µg PAH/kg Soil	8.0E-01	8.0E-01	8.0E-01	8.0E-01
Dust	µgPAH/m^3 Air	4.8E-08	4.8E-08	4.8E-08	4.8E-08
Dust-tilling	µg PAH/m^3 Air	2.3E-04	2.3E-04	2.3E-04	2.3E-04

note: cited from Concord, 1991

Table 3.9 shows authentic data collected from the on-site experiment for the soil PAH concentrations designated as Soil, along with the dust and dust-tilling concentrations calculated by applying the dust and dust-tilling source factor to the soil PAH concentrations. A comparison of the base estimate case PAH estimate (Concord, 1991) to the field data shows the extent of over-estimation of PAH exposure *via* airborne particulates (Table 3.10).

Table 3.9 Measured Contaminant Concentrations for Direct Exposure Pathways of Receptors at the Borradaile Site - Field Estimate Case

Pathway	Units	Benzo(a)pyrene	Phenanthrene	Chrysene	Naphthalene
Soil	µg PAH/kg Soil	1.4E+01	2.7E+01	3.2E+01	1.9E+01
Dust	µg PAH/m^3 Air	8.4E-07	2.0E-06	2.0E-06	1.0E-06
Dust-tilling	µg PAH/m^3 Air	4.0E-03	8.0E-03	9.0E-03	5.5E-03

note: the soil concentrations were measured and the dust and dust-tilling data were calculated from the Concord (1991) stated assumptions.

Table 3.10 Base Estimate Case: Field Estimate Case Ratio

Ratio- Base Estimate Case:Field Estimate Case				
Pathway	Naphthalene	Phenanthrene	Chrysene	Benzo(a)pyrene
Soil	342	240	203	464
Dust	390	195	195	9750
Dust-tilling	345	238	211	475

The limitation of using O&G analysis for estimating PAHs is that the soxhlet extraction/gravimetric method (APHA,1989) is strictly empirical and not specifically related to PAHs. The method is sensitive to sample preparation, rate and time of extraction and the drying time. The "O&G" analysis includes extraction of varying components unrelated to PAHs (Pollard and Hrudey, 1992):

-waste from organic and organo-metallic compounds;

-high molecular weight and branched alkanes;

-biogenic fatty acids and esters;

-triglycerides oils and plant derived lipids; and

-plant based pheophytones (eg. chlorophyl A).

Thus the limitation of risk assessment based on O&G is that this measurement of non-specific constituents provides no information on the PAH composition of hydrocarbons in contaminated soils. Therefore, the assumption of a linear correlation between O&G and indicator PAH content, a PAH source factor is not reliable.

This study has only re-evaluated ingestion of produce, soil and dust, dermal exposure to soil and inhalation to dust. No field data were obtained on PAH content of beef, milk and water, so comparison with the Concord dose estimates were not performed for these exposure routes.

Generally, conservative assumptions are made in exposure modelling so that exposure estimates will be higher than actual exposures (Kostecki and Calabrese, 1990, 1991). Taken to extremes, such an approach can lead to gross overestimates of exposure or portray people with unrealistic lifestyles. The adult receptor has a body mass of 70 kg; a daily inhalation rate of 23 m^3/day based on 8 hours of light activity, 8 hours of non-

occupational activity and 8 hours of rest and a daily produce consumption of 0.092 kg/day. The receptor was assumed to spend all of his/her time either in the house or in the yard. Activities include gardening and tilling the soil.

The adult was assumed to maintain a garden on the site which provided 100% of the produce consumed (Concord, 1991). The relative importance of ingestion of produce to the dose estimates was dependent on the calculated plant uptake factors. The risk assessment used a two mechanism approach to calculate plant uptake: uptake via roots which is dependent on K_{ow} (see Chapter 1) and foliar deposition predominates for highly volatile PAHs (Wild and Jones, 1992c). As a simplifying and conservative assumption, the hypothetical plant had the combined characteristics of a root crop and leafy vegetable (Concord, 1991).

The relative contributions of various direct (i.e. ingestion of soil, dermal and inhalation exposures) and indirect exposure (i.e. ingestion of garden produce) routes can be assessed. Tables 3.11 to 3.14 show the calculated and summed dose estimates delivered to the specific adult receptor for each of the four PAHs with each of the exposure cases.

For the exposure routes considered the ingestion of garden produce was the predominant exposure to PAHs. The vegetative uptake of PAHs in the real estimate case showed that for both receptors, naphthalene (39%) and phenanthrene (49%) are the major contributors of the PAH load. The relative distribution is also seen with the estimated exposures for the base case and lower estimate case. The physico-chemical properties of the four PAHs investigated also show that naphthalene and phenanthrene would be the most likely PAHs to be absorbed due to high volatility. Comparing the relative percent

Table 3.11 Chronic Dose Estimates of Naphthalene for Adult Receptor

	Naphthalene Contaminant		
Routes of Intake	Base Estimate Case µg/kg/day	Lower Estimate Case µg/kg/day	Field Estimate Case µg/kg/day
CHRONIC EXPOSURES**			
Ingestion of Garden Produce	1.7E+00*	2.0E-04*	2.8E-02*
Ingestion of Soil-continuous	1.5E-03	1.9E-07	4.0E-06
Ingestion of Soil-gardening	7.6E-04	9.4E-08	2.0E-06
Ingestion of Soil-tilling	3.2E-04	3.9E-08	9.3E-07
Ingestion of Dust-continuous	3.2E-05	3.9E-09	8.2E-08
Ingestion of Dust-tilling	1.8E-03	2.3E-07	5.0E-06
Dermal Exposure to Soil-gardening	1.4E-03	1.8E-07	4.0E-06
Dermal Exposure to Soil-tilling	1.8E-03	2.2E-07	5.0E-06
Inhalation of Dust-continuous	3.2E-05	3.9E-09	8.2E-08
Inhalation of Dust-tilling	1.8E-03	2.3E-07	5.0E-06
Total Ingestion	1.7E+00*	2.0E-04*	2.8E-02*
Total Dermal	3.2E-03	4.0E-07	9.0E-06
Total Inhalation	1.8E-03	2.3E-07	5.0E-06
TOTAL CHRONIC DOSE	1.7E+00	2.0E-04	2.8E-02

note: * dominates the total chronic dose
**these estimates do no include inhalation exposure to vapor phase naphthalene or to secondary products such as beef or milk

Table 3.12 Chronic Dose Estimates of Phenanthrene for Adult Receptor

Routes of Intake	Phenanthrene Contaminant Base Estimate Case µg/kg/day	Lower Estimate Case µg/kg/day	Field Estimate Case µg/kg/day
CHRONIC EXPOSURES**			
Ingestion of Garden Produce	4.7E-01*	5.8E-05*	2.2E-02*
Ingestion of Soil-continuous	1.5E-03	1.9E-07	6.0E-06
Ingestion of Soil-gardening	7.6E-04	9.4E-08	3.0E-06
Ingestion of Soil-tilling	3.2E-04	3.9E-08	1.0E-06
Ingestion of Dust-continuous	3.2E-05	3.9E-09	8.0E-06
Ingestion of Dust-tilling	1.8E-03	2.3E-07	
Dermal Exposure to Soil-gardening	1.4E-03	1.8E-07	6.0E-06
Dermal Exposure to Soil-tilling	1.8E-03	2.2E-07	7.0E-06
Inhalation of Dust-continuous	3.2E-05	3.9E-09	1.6E-07
Inhalation of Dust-tilling	1.8E-03	2.3E-07	8.0E-06
Total Ingestion	4.7E-01*	5.9E-05*	2.2E-02*
Total Dermal	3.2E-03	4.0E-07	1.3E-05
Total Inhalation	1.8E-03	2.3E-07	8.0E-06
TOTAL CHRONIC DOSE	4.8E-01	6.0E-05	2.2E-02

note: * dominates the total chronic dose
** these estimates do no include inhalation exposure to vapor phase phenanthrene or to secondary products such as beef or milk

Table 3.13 Chronic Dose Estimates of Chrysene for Adult Receptor

Routes of Intake	Chrysene Contaminant Base Estimate Case µg/kg/day	Lower Estimate Case µg/kg/day	Field Estimate Case µg/kg/day
CHRONIC EXPOSURES**			
Ingestion of Garden Produce	1.3E-01*	1.6E-05*	5.2E-03*
Ingestion of Soil-continuous	1.5E-03	1.9E-07	8.0E-06
Ingestion of Soil-gardening	7.6E-04	9.4E-08	4.0E-06
Ingestion of Soil-tilling	3.2E-04	3.9E-08	2.0E-06
Ingestion of Dust-continuous	3.2E-05	3.9E-09	1.6E-07
Ingestion of Dust-tilling	1.8E-03	2.3E-07	9.0E-06
Dermal Exposure to Soil-gardening	1.4E-03	1.8E-07	7.0E-06
Dermal Exposure to Soil-tilling	1.8E-03	2.2E-07	9.0E-06
Inhalation of Dust-continuous	3.2E-05	3.9E-09	1.6E-07
Inhalation of Dust-tilling	1.8E-03	2.3E-07	9.0E-06
Total Ingestion	1.3E-01*	1.7E-05*	5.2E-03*
Total Dermal	3.2E-03	4.0E-07	1.6E-05
Total Inhalation	1.8E-03	2.3E-07	9.0E-06
TOTAL CHRONIC DOSE	1.4E-01	1.8E-05	5.2E-03

note: * dominates the total chronic dose
** these estimates do not include inhalation exposure to vapor phase chrysene or to secondary products such as beef or milk

Table 3.14 Chronic Dose Estimates of Benzo(a)pyrene for Adult Receptor

Routes of Intake	Benzo(a)pyrene Contaminant Base Estimate Case µg/kg/day	Lower Estimate Case µg/kg/day	Field Estimate Case µg/kg/day
CHRONIC EXPOSURES**			
Ingestion of Garden Produce	8.0E-02*	9.9E-06*	2.6E-03*
Ingestion of Soil-continuous	1.5E-03	1.9E-07	3.0E-06
Ingestion of Soil-gardening	7.6E-04	9.4E-08	2.0E-06
Ingestion of Soil-tilling	3.2E-04	3.9E-08	6.8E-07
Ingestion of Dust-continuous	3.2E-05	3.9E-09	6.9E-08
Ingestion of Dust-tilling	1.8E-03	2.3E-07	4.0E-06
Dermal Exposure to Soil-gardening	1.4E-03	1.8E-07	3.0E-06
Dermal Exposure to Soil-tilling	1.8E-03	2.2E-07	4.0E-06
Inhalation of Dust-continuous	3.2E-05	3.9E-09	6.9E-08
Inhalation of Dust-tilling	1.8E-03	2.3E-07	4.0E-06
Total Ingestion	8.4E-02*	1.0E-05*	2.6E-03*
Total Dermal	3.2E-03	4.0E-07	7.0E-06
Total Inhalation	1.8E-03	2.3E-07	4.0E-06
TOTAL CHRONIC DOSE	9.0E-02	1.0E-05	2.6E-03

note: * dominates the total chronic dose
** these estimates do not include inhalation exposure to vapor phase benzo(a)pyrene or to secondary products such as beef or milk

Table 3.15 Percent Exposure Contribution to the Chronic Dose* of each PAH for the Adult Receptor- Base/Lower Estimate Case

	Percent Contributions to Total PAH Exposure from each Route			
Exposure Route	Naphthalene	Phenanthrene	Chrysene	Benzo(a)pyrene
Produce Ingestion	99.5	98.0	93.3	89.5
Soil Ingestion	0.20	0.93	3.10	4.90
Dermal	0.18	0.64	2.20	3.40
Inhalation	0.12	0.43	1.40	2.20

note: * these exposure estimates do not include inhalation exposure to vapor phase PAHs or to secondary products such as beef or milk

Table 3.16 Percent Exposure Contributions to the Chronic Dose* of each PAH for the Adult Receptor - Field Estimate Case

	Percent Contributions to Total PAH Exposure from each Route			
Exposure Route	Naphthalene	Phenanthrene	Chrysene	Benzo(a)pyrene
Produce Ingestion	99.9	99.8	99.1	99.2
Soil Ingestion	0.04	0.08	0.44	0.37
Dermal	0.03	0.06	0.30	0.27
Inhalation	0.03	0.06	0.16	0.16

note: * these exposure estimates do not include inhalation exposure to vapor phase PAHs or to secondary products such as beef or milk

contributions from each of the exposure routes to the chronic dose show ingestion to comprise a dominating 90+% of the load (Table 3.15 and 3.16). The distribution of PAHs within each of the exposure routes show benzo(a)pyrene to comprise only 5% of the PAH load. A typical diet estimated by the EPA results in an average benzo(a)pyrene intake of 50 ng/day (Post *et al.*, 1993). With the field case, ingestion of produce contributes to a daily benzo(a)pyrene intake of 182 ng for the adult receptor.

The actual risk will be less significant than that estimated in the base case, since the risk assessment deliberately overlooked any losses of substances during food preparation. The content of PAH in food not only depends upon its source, but also the style of cooking and personal eating habits (Howard and Fazis, 1983 and Lijinsky, 1991). The ingestion of benzo(a)pyrene and total PAH from food has been estimated to range from 5 to 1170 ng/day and 1600 to 16000 ng/day, respectively (Santodonato, 1981 and Menzie *et al.*, 1992).

Direct soil ingestion exposures arise from the inadvertant or deliberate ingestion of soil and dust. The Centre for Disease Control (CDC) has assumed that the soil intake for those ages 17 to 70 years is 100 mg/day (Kostecki and Calabrese, 1989). Ingestion of soil and dust through activities such as gardening and tilling the soil is less of a risk factor than ingestion of garden produce, but more significant than dermal or inhalation exposures. A comparison of the chronic dose estimates for the adult under the base estimate case, lower estimate case and field estimate case (Table 3.11 to 3.14), show the field estimate case to lie between the extreme of the base estimate case and the lower estimate case. The relative percent contribution of soil ingestion to the chronic adult dose ranged from 0.04% to 4.9%. The contribution of soil ingestion to the chronic dose increased with the larger, more persistent PAHs as chrysene and benzo(a)pyrene. The base estimate case calculations

show a significant soil ingestion contribution from chrysene and benzo(a)pyrene which contrasts the field estimate case result, which shows that under realistic conditions uptake of contaminants by soil ingestion was less probable.

Quantitative estimates of the dermal uptake of chemicals from dust or soil contain more uncertainty than estimates for other routes of entry (Hawley, 1983). Dermal absorption of PAHs from soil and dust depends on the area of contact, the duration of contact, the sorption capacity to the soil matrix and the ability of PAHs to penetrate the skin. Dermal bioavailability was assumed to be 10% for the Borradaile risk assessment (Kenaga, 1980). Most dermal bioavailability data for contaminated soil have been obtained from animal and in-vitro test systems. This introduces a significant uncertainty, therefore safety factors have been implemented to overestimate uptake. This uncertainty factor is probably unnecessary in most cases, since human skin has shown to be 10% less permeable to xenobiotics than the skin of rabbits and mice (Kostecki and Calabrese, 1989).

EPA has considered dermal exposure to be an exposure route of relatively less significance, with the possible exception of certain occupational situations (USEPA, 1982). Dermal exposure with all dose estimates, *i.e.* results from base, field and lower estimate case in this study, represents less than 5% (range 0.03 to 3.5%) of the total chronic dose. The predominating PAHs that were exposed to the receptors were phenanthrene (29%) and chrysene (36%), with naphthalene and benzo(a)pyrene contributing 16% and 21%, respectively. The adult exposure through the contact of skin was shown to be relatively insignificant under the given activities carried out by the receptor.

Inhalation exposures are continuous, as a result, of the presence of total suspended particulates (TSP) and vapors in the air. The degree of inhalation hazard will generally be dictated by the volatility of the chemical, the proximity of the population to the site and the

amount of dust generated at the site. The original risk assessment (Concord, 1991) considered suspended particulates as the only source of PAHs for inhalation exposure from this particular site. Vapor phase contribution to inhalation exposure was not evaluated in the dose estimate calculations. Under the greenhouse growth experiment (Chapter 2) conditions, the fresh creosote produced substantial levels of naphthalene, phenanthrene and chrysene, however, benzo(a)pyrene levels were near the analysis detection limit of 1ppb. The input of the reported benzo(a)pryene levels from the greenhouse (Figure 2.13) to calculate exposure for the adult receptor on-site resulted in substantial increase of the overall inhalation exposure (2.0 μg/kg/d). However, on-site levels of benzo(a)pyrene would not be comparable to the levels found in the greenhouse experiment, using a fresh source of PAHs under confined conditions. It must be emphasized that inhalation exposures should include exposure *via* suspended particulates and vapors.

The relative percent contribution of inhalation exposure to the total chronic dose was similar to the pattern shown for dermal contact. The inhalation exposure contributes to less than 5% (range 0.03 to 4.3%) of the total chronic dose estimate with a daily intake of 0.28 ng for the adult receptor. Smoking has been indicated to be the most significant pathway of PAH exposure, contributing an average daily benzo(a)pyrene intake of 600 ng (based on an average of 25 cigarettes per day). Daily benzo(a)pyrene doses *via* inhalation of ambient air were estimated by EPA to range from 20 to 2000 ng (urban) and 0.2 to 200 ng (rural) (Post *et al.*, 1993). Therefore the Borradaile site exposure to PAHs is significantly less than that from smoking.

This overview shows that direct and indirect pathways have different PAH contributions for each of the exposure routes. Direct exposure has shown a predominance to phenanthrene and chrysene as the main components. Indirect exposure by produce

ingestion indicated the predominance of naphthalene and phenanthrene as the contributing factor to PAH uptake.

Comparing the total cancer risk for the base estimate case and lower estimate gave a range of 1.0×10^{-3} to 1.2×10^{-7} lifetime cancer risk.with the base estimate case being 1 to 3 orders of magnitude greater than the *de minimis* risk range of 1×10^{-6} to 1×10^{-5} (Concord, 1991). The base case total cancer risk was judged to be unacceptable by the criteria used in this risk assessment. The level of risk of 1.2×10^{-7} for the lower estimate was considered acceptable, since it was below the *de minimis* level. Even though the EPA generally uses the FDA precedent of 10^{-6}, when relatively few people are exposed, the EPA often chooses not to require reductions in exposure when the calculated risks are as high as 10^{-4} and even 10^{-3}.

The human health risk with respect to benzo(a)pyrene was calculated for the field estimate case to compare to the calculated base estimate case. The maximally exposed receptor for the field estimate case shows a total risk of 3.1×10^{-5} which is a *de minimis* risk for the small number of exposed individuals (Table 3.20).

Another indicator of risk in such a human health risk assessment is the Hazard Quotient. The Hazard Quotient is used to assess systemic effects for substances with thresholds or no observable adverse effects levels. The Hazard Quotient is the ratio of the estimated dose to the acceptable daily intake (ADI). The ADI's acceptability is based on a level presumed to pose no likelihood of causing an adverse health effect . The values for the calculated Hazard Quotient were all below 0.1, indicating low levels of concern for the three PAHs other than benzo(a)pyrene (Tables 3.17 to 3.20).

Table 3.17 Health Risk Summary for Maximal Lifetime Exposure of Naphthalene at the Borradaile Site

Parameters	Base Estimate Case	Lower Estimate Case	Field Estimate Case
Risk Factors (mg/kg/day)			
Virtually safe dose	na	na	na
Acceptable daily intake (ADI)	1.4E-01	1.4E-01	1.4E-01
Slope Factors (1/mg/kg/day)			
Oral (ingestion + dermal)	na	na	na
Inhalation	na	na	na
Chronic Dosage (mg/kg/day)			
Total Ingestion	1.7E-03	2.0E-07	2.8E-05
Total Dermal	3.2E-06	4.0E-10	9.0E-09
Total Oral	1.7E-03	2.0E-07	2.8E-05
Total Inhalation	1.8E-06	2.3E-10	5.0E-09
Total Dose	1.7E-03	2.0E-07	2.8E-05
Risk			
Total Oral	na	na	na
Total Inhalation	na	na	na
Total Risk	na	na	na
Hazard Quotient (Total Dose/ADI)	1.2E-02	1.4E-06	2.0E-04

note: na = not applicable

Table 3.18 Health Risk Summary for Maximal Lifetime Exposure of Phenanthrene at the Borradaile Site

Parameters	Base Estimate Case	Lower Estimate Case	Field Estimate Case
Risk Factors (mg/kg/day)			
Virtually safe dose	na	na	na
Acceptable daily intake (ADI)	4.0E-02	4.0E-02	4.0E-02
Slope Factors (1/mg/kg/day)			
Oral (ingestion + dermal)	na	na	na
Inhalation	na	na	na
Chronic Dosage (mg/kg/day)			
Total Ingestion	4.7E-04	5.9E-08	2.2E-05
Total Dermal	3.2E-06	4.0E-10	1.3E-08
Total Oral	4.7E-04	5.9E-08	2.2E-05
Total Inhalation	1.8E-06	2.3E-10	8.0E-09
Total Dose	4.7E-04	5.9E-08	2.2E-05
Risk			
Total Oral	na	na	na
Total Inhalation	na	na	na
Total Risk	na	na	na
Hazard Quotient (Total Dose/ADI)	1.2E-02	1.5E-06	5.5E-04

note: na = not applicable

Table 3.19 Health Risk Summary for Maximal Lifetime Exposure of Chrysene at the Borradaile Site

Parameters	Base Estimate Case	Lower Estimate Case	Field Estimate Case
Risk Factors (mg/kg/day)			
Virtually safe dose	na	na	na
Acceptable daily intake (ADI)	1.0E-02	1.0E-02	1.0E-02
Slope Factors (1/mg/kg/day)			
Oral (ingestion + dermal)	na	na	na
Inhalation	na	na	na
Chronic Dosage (mg/kg/day)			
Total Ingestion	1.3E-04	1.7E-08	5.2E-06
Total Dermal	3.2E-06	4.0E-10	1.6E-08
Total Oral	1.3E-04	1.7E-08	5.2E-06
Total Inhalation	1.8E-06	2.3E-10	9.0E-09
Total Dose	1.3E-04	1.7E-08	5.2E-06
Risk			
Total Oral	na	na	na
Total Inhalation	na	na	na
Total Risk	na	na	na
Hazard Quotient (Total Dose/ADI)	1.3E-02	1.7E-06	5.2E-04

note: na = not applicable

Table 3.20 Health Risk Summary for Maximal Lifetime Exposure of Benzo(a)pyrene at the Borradaile Site

Parameters	Base Estimate Case	Lower Estimate Case	Field Estimate Case
Risk Factors (mg/kg/day)			
Virtually safe dose	8.7E-08	8.7E-08	8.7E-08
Acceptable daily intake (ADI)	na	na	na
Slope Factors (1/mg/kg/day)			
Oral (ingestion + dermal)	1.2E+01	1.2E+01	1.2E+01
Inhalation	6.1E+00	6.1E+00	6.1E+00
Chronic Dosage (mg/kg/day)			
Total Ingestion	8.4E-05	1.0E-08	2.6E-06
Total Dermal	3.2E-06	4.0E-10	7.0E-09
Total Oral	8.7E-05	1.0E-08	2.6E-06
Total Inhalation	1.9E-06	2.3E-10	4.0E-09
Total Dose	8.9E-05	1.0E-08	2.6E-06
Risk			
Total Oral	1.0E-03	1.2E-07	3.1E-05
Total Inhalation	1.2E-05	1.0E-09	2.4E-08
Total Risk	1.0E-03	1.2E-07	3.1E-05
Hazard Quotient (Total Dose/ADI)	na	na	na

note: na = not applicable

The Borradaile risk assessment focussed primarily on a single contaminant, benzo(a)pyrene for assessing human health effects. However, the contaminant on site was a heavy oil mixture. Evaluating the risks of mixed exposures presents problems not encountered with individual exposures (Lewtas, 1989). For example, not all of the components of a mixture may be known. Even if the components are identified, the composition of the mixture may vary. Important complicating factors are the possibility of interaction and non-additive synergistic effects among the different components of a given mixture (Krewski *et al.*, 1989).

In realistic situations, the public is exposed to complex mixtures of chemical agents at low concentrations. The compositions of such mixtures will vary depending on the different human activities and exposure circumstances. However, toxicological studies, contrary to epidemiological studies, are carried out in the laboratory using single compounds at high doses that guarantee the observation of negative effects. Therefore, assumptions and interpretations based on these type of results should be carefully used (Newill, 1989).

The EPA risk assessment methods differ widely in their accuracy and degree of biological justification. Assessments are usually based on the "most toxic" components of a mixture. This may lead to inaccurate assessments, due partially to unclear judgement used in the selection of the chemicals. The best approach, with the highest biological justification, is to use data developed by testing a complete given mixture, or results based on a toxicologically similar mixture.

Current research in risk assessment methodologies include (Newill, 1989):

- "development of simple statistical risk models for multiple toxic endpoints;

- classification of mixtures based on interaction mechanisms;

- refinement and validation of short term and in vitro assays for comparative potency approaches using whole mixture data;

- experimental studies to determine if significant synergism can occur near the no-effects levels of component chemicals; and

- improved methodology for using epidemiological studies, to directly incorporate the mixtures exposures instead of merely controlling the mixtures exposures."

A potential approach that can be used in risk assessments to efficiently assess levels of contaminants in plants is to sample indigenous vegetation from the site. Table 3.21 reports the levels of PAHs analyzed in three selected weeds and their corresponding soils. The perennial weed, *Triglochin maritima* represents a long-term exposure, while the *Salicornia rubra A. nels*, an annual plant serves as a measure of seasonal exposure. Table 3.22 shows the O&G levels found in the selected native vegetation from the site levels that range from high oil contamination to levels that would exceed anything conceivable for a garden.. The PAH source factor used by Concord (1991) applied to the *Triglochin maritima* O&G level gave an estimated PAH soil concentration of 121 μg/g compared to a measured average PAH concentration of 4.0 μg/g. Table 3.23 shows a comparison of PAH dosage using native vegetation as a surrogate for garden produce in the risk assessment at hazardous sites. Because the native vegetation was sampled from soil that was visibly and grossly contaminated with oil compared with any soil likely to be used in a garden, the resulting vegetation PAH levels represent an upper bound on conceivable exposures. Realistic exposures would be expected to be much lower, as determined with

Table 3.21 Borradaile PAH Concentrations of Selected Native Weeds and their Corresponding Soil Concentrations (µg/g dry wt basis)

Sample Identification	*Triglochin Maritima* #1 (Pit #7)	*Triglochin Maritima* #2 (Pit #7)	*Triglochin Maritima* #3 (Pit #7)	***Triglochin Maritima*** **(#1,2,3)**	Wild Barley (*Hordeum jabatum L.*) (Pit #6)	*Salicornia rubra A. nels.* (Pit#6)	**Pit #6 (Wild Barley& *Salicornia rubra A. nels.*) (soil sample)**
		mean (SD)		**(soil sample)**			
2-ring							
naphthalene	0.020	0.026 (0.005)	0.020	**0.48**	0.098	0.011	**0.049**
3-ring							
acenaphthylene	nd	nd	nd	**nd**	nd	nd	**nd**
acenaphthene	0.058	0.088 (0.002)	0.019	**0.84**	0.044	0.016	**0.009**
fluorene	0.066	0.011 (0.0003)	0.004	**5.02**	0.317	0.001	**0.011**
phenanthrene	0.192	0.093 (0.004)	0.065	**16.1**	0.524	0.013	**0.059**
anthracene	0.101	0.009 (0.004)	0.004	**8.48**	0.125	0.006	**0.015**
4-ring							
fluoranthene	0.269	0.850 (0.012)	0.089	**7.16**	0.028	0.008	**0.016**
pyrene	0.202	0.146 (0.015)	0.076	**5.19**	0.045	0.004	**0.024**
benzo(a)anthracene	0.056			**2.31**			
chrysene	0.158	0.284 (0.012)	0.236	**6.00**	0.090	0.007	**0.076**
5-ring							
benzo(b+k)fluoranthene	0.143	0.245 (0.029)	0.196	**4.42**	nd	nd	**0.082**
benzo(a)pyrene	0.060	0.060 (0.016)	0.061	**0.58**	nd	0.001	**0.029**
dibenzo(a,h)anthracene	0.010	0.027 (0.003)	0.017	**0.54**	nd	0.006	**0.015**
6-ring							
indeno(1,2,3,-cd)pyrene	0.600	0.124 (0.002)	0.085	**1.68**	0.031	0.005	**0.061**
benzo(ghi)perylene	0.058	0.095 (0.003)	0.076	**1.80**	0.019	0.004	**0.066**

note: *mean and standard deviation of multiple analysis of *Triglochin maritima*

Table 3.21 Continued

Sample Identification	Wild Barley (*Hordeum jabatum L.*) #1 (Pit #1)	Pit #1 (Wild Barley #1) (soil sample)	Wild Barley (*Hordeum jabatum L.*) #2 (Pit #1) mean {SD}	Pit #1 (Wild Barley #2) (soil sample)
2-ring				
naphthalene	0.391 {0.023}	1.17	0.310 {0.003}	0.158
3-ring				
acenaphthylene	nd	nd	nd	nd
acenaphthene	0.513 {0.025}	0.123	0.557 {0.029}	0.214
fluorene	0.384 {0.009}	0.120	0.369 {0.064}	0.050
phenanthrene	0.567 {0.030}	0.143	0.463 {0.016}	0.033
anthracene	0.108 {0.015}	0.079	0.161 {0.005}	0.005
4-ring				
fluoranthene	0.137 {0.038}	0.346	0.089 {0.003}	0.0056
pyrene	0.400 {0.031}	0.397	0.069 {0.023}	0.02
benzo(a)anthracene		0.138		
chrysene	0.986 {0.113}	0.707	0.184 {0.027}	0.060
5-ring				
benzo(b+k)fluoranthene	0.670 {0.008}	0.569	0.159 {0.031}	0.1389
benzo(a)pyrene	0.158 {0.041}	0.167	0.030 {0.002}	0.04
dibenzo(a,h)anthracene	0.062 {0.003}	0.083	0.024 {0.014}	0.0308
6-ring				
indeno(1,2,3,-cd)pyrene	0.351 {0.008}	0.259	0.066 {0.007}	0.0786
benzo(ghi)perylene	0.425 {0.034}	0.324	0.058 {0.013}	0.063

Table 3.22 Oil and Grease Content of the Borradaile Weed Soils

Sample ID	Oil and Grease (µg/g dry weight basis)
Triglochin maritima (#1,2,3)	483000
Pit #6 (Wild Barley & Salicornia rubra A. nels.	17400
Pit #1 (Wild Barley #1)	52200
Pit #1 (Wild Barley #2)	7600

Table 3.23 Chronic Dose Estimates using Native Weeds from the Borradaile Site for the Adult Receptor

	Benzo(a)pyrene Contaminant				
Routes of Intake	Base Estimate Case	Lower Estimate Case	Field Estimate Case	Longterm Estimate *T. maritima*	Short term Estimate *S. rubra A nels*
	µg/kg/day	µg/kg/day	µg/kg/day	µg/kg/day	µg/kg/day
CHRONIC EXPOSURES					
Ingestion of Garden Produce	8.0E-02	9.9E-06	2.6E-03	7.9E-02	1.3E-03
Ingestion of Soil-continuous	1.5E-03	1.9E-07	3.0E-06	1.4E-04	6.8E-06
Ingestion of Soil-gardening	7.6E-04	9.4E-08	2.0E-06	6.8E-05	3.4E-06
Ingestion of Soil-tilling	3.2E-04	3.9E-08	6.8E-07	2.8E-05	1.4E-06
Ingestion of Dust-continuous	3.2E-05	3.9E-09	6.9E-08	2.9E-06	1.6E-07
Ingestion of Dust-tilling	1.8E-03	2.3E-07	4.0E-06	1.7E-04	8.2E-06
Dermal Exposure to Soil-gardening	1.4E-03	1.8E-07	3.0E-06	1.3E-04	6.4E-06
Dermal Exposure to Soil-tilling	1.8E-03	2.2E-07	4.0E-06	1.6E-04	8.0E-06
Inhalation of Dust-continuous	3.2E-05	3.9E-09	6.9E-08	2.9E-06	1.6E-07
Inhalation of Dust-tilling	1.8E-03	2.3E-07	4.0E-06	1.7E-04	8.2E-06
Total Ingestion	8.4E-02	1.0E-05	2.6E-03	7.9E-02	1.3E-03
Total Dermal	3.0E-03	4.0E-07	7.0E-06	2.9E-04	4.4E-05
Total Inhalation	2.0E-03	2.3E-07	4.0E-06	1.7E-04	8.4E-06
TOTAL CHRONIC DOSE	9.0E-02	1.0E-05	2.6E-03	7.9E-02	1.3E-03

the field growth experiments.

The benzo(a)pyrene concentration in *Triglochin maritima* provided a chronic dose of 7.9 $x10^{-2}$ µg/kg/day, corresponding well to the base estimate case of 9.0 x 10^{-2} µg/kg/day. The *Triglochin maritima* weed, soil concentrations and the dose estimates for the three indicator PAHs - naphthalene, phenanthrene and benzo(a)pyrene are higher than the real estimate case, but do not exceed the corresponding over-estimated base estimate case values despite being found growing in soil with an oil and grease concentration of 483,000µg/g. Chrysene does exceed the vegetation concentration of the estimated base estimate case. The *Salicornia rubra* provided a better dose estimation to the field estimate case rather than the lower estimate case. In any case, collection of vegetation from highly contaminated locations at the site in question, can provide useful information that can be used to interpret the human health risk assessment.

The plant uptake models (Appendix D) used for the estimation of the PAH concentration in vegetation in the risk assessment by Concord, were based on the summation of the extent of contamination from foliar deposition and uptake *via* roots.

The comparison of results in Table 3.24, show that the main source of over-estimation (Concord, 1991) arose with the high estimates for the soil PAH levels used for the original risk assessment compared with the authentic measured values from the Borradaile site. The models for plant uptake of PAHs used by Concord actually underestimated plant PAH levels using field soil PAH concentrations compared with levels measured in the plants grown in the field. This finding may reflect the experimental approach used for growing the plants on-site. In the case of the covered plants, this condition would maximize the importance of volatilization compared with open exposure in a garden.

Table 3.24 Comparison of Actual to Estimated Data in the Plant Uptake Models (μg/kg)

PAH	Concord Estimated Soil Concentration. (μg/kg) (Table 3.7)	Calculated Vegetation Concentration using Concord Estimated Soil Concentration (μg/kg) (Table 3.5)	Field Soil Concentration from Borr. Site (μg/kg) (Table 3.9)	Calculated Vegetation Concentration using Field Soil Concentration (μg/kg)	Field Grown Vegetation from Borr. Site (μg/kg) (Table 3.6)
naphthalene	6500	1300	19.0	3.66	21.0
phenanthrene	6500	360	27.0	1.48	17.0
chrysene	6500	96	32.0	0.48	4.0
benzo(a)pyrene	6500	61	14.0	0.12	2.0

Rigorous chemical analysis and knowledge of the properties of PAHs are required to allow a realistic judgement regarding the behavior of individual PAHs and the possible exposure and corresponding risk from contaminants at a specific hazardous waste site.

3.3 Conclusions

A previous risk assessment performed on the Borradaile site estimated unacceptable risk to humans. The level of risk was stated to be approximately four times the level experienced by a typical smoker. The calculations were based on many assumptions and limited site characterization data . On-site field data was therefore collected and used to validate the risk estimates from the original human health risk assessment.

For the exposure routes considered, ingestion of garden produce was the predominant exposure to PAHs. PAH exposures *via* ingestion of garden produce and exposure to soil were considerably lower for plants grown in soil on the site than was estimated by the original health risk assessment.

The lifetime cancer risk for benzo(a)pyrene from the field estimate case was 3.1×10^{-5}, a value within the considered acceptable range for individual exposures compared with the unacceptable estimated value of 1.0×10^{-3} from the original health risk assessment. The field estimate case was two orders of magnitude lower than that of the upper bound risk estimate. The main source of over-estimation of PAH contamination for the original risk assessment was the estimated PAH contamination of the soil.

Analysis of native vegetation growing in highly contaminated soil at an oil contaminated site can provide a useful indication of plausible upper bound for vegetation contamination by PAHs. The perennial weed*Triglochin maritima* represents a longterm exposure and was found to be comparable to the upper bound dose estimates. However, realistic exposures would be expected to be much lower, as determined with the field growth experiments.

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4.0 Summary of Conclusions

4.0 Summary of Conclusions

A previous Concord (1991) risk assessment performed on the Borradaile site estimated unacceptable risk to humans. It was stated that the exposure to benzo(a)pyrene, a PAH to be a potential carcinogen was approximately four times the level experienced by a typical smoker. The calculations were based on many assumptions and limited site characterization data. Of specific concern were the assumptions relating to PAH uptake by vegetation. As a result, two objectives were established:

- to deal with the question of PAH exposure routes to plants by conducting plant growth greenhouse experiments using PAH creosote contaminated soils and

  to evaluate the PAH level of on-site soil and vegetation from Borradaile and to assess the validity of the original risk estimates.

The greenhouse growth experiment shows substantial transfer of PAHs out of the upper soil layer throughout the duration of the experiment. Some of these losses or transfer can be attributed to volatilization and by leaching. The 3- and 4-ring PAHs dominated the PAH losses from the soil. The larger 5- and 6-ring PAHs were present at low levels and tended to be more resistant to loss due to their large molecular size and low solubility.

The highest exposure of PAH levels to barley and lettuce was shown to be under the condition where the plants were covered but were exposed to the soil. This suggests that volatilization of PAH vapors from the soil plays a role in foliar uptake. The levels of PAH were also greater in the lettuce than barley under the same treatment. This was

explained as a result of the larger leaf surface area and growing at ground level allowing for more efficient entrapment of the volatiles and semi-volatile PAHs. Under the treatment, where the plants were covered but the soil was lined to control volatilization, there was PAH uptake suggesting that root uptake is still important.

The carrot allowed a closer observation of uptake within a root. The PAH concentrations detected in the carrot root peel were all substantially higher than that in the core. This result shows the gradient of PAH in the outer tissue near the contaminated soil compared with the inner core tissue. In both the cores and peels the PAH burden was dominated by the lower molecular weight compounds. Approximately 70 to 80% of the PAH burden found in the carrots was associated with the peel.

The Level I fugacity model was tested with the data collected from the greenhouse experiment to predict the PAH concentrations within the plant compartments. This model assumes that the plant/soil system is in equilibrium. Under the growth conditions in the greenhouse, the fugacity model shows that equilibrium was not achieved to allow the use of the equilibrium model.

In the re-evaluation of the original risk assessment using measured on-site soil and vegetation concentrations, ingestion of garden produce was the predominant exposure to PAHs. The ingestion of produce contributed to over 95% of the total chronic dose. PAH exposures *via* ingestion of garden produce and exposure to soil were considerably lower for plants grown on-site in soil from the site than was estimated by the original health risk assessment.

The lifetime cancer risk for benzo(a)pyrene from the field estimate case was 3.1×10^{-5}, a value within the considered acceptable range of 1×10^{-5} to 1×1^{-6} for individual

exposures. The original health risk assessment estimated a risk of 1.0×10^{-3} which was two orders of magnitude higher than that of the field estimate case. The main source of over-estimation of PAH contamination for the original risk assessment was the estimated PAH contamination of the soil.

When it comes to human health risk assessment, too many assumptions may dilute the significance of specific parameters. Site characterization can provide a more realistic picture of potential health risk than that produced by relying on a series of assumptions. Accurate measurements should be a requirement rather than estimates based on models and questionable assumptions.

Appendix A

Appendix A

Recovery Analysis of Soil - Soxhlet Extraction

See Chapter 2

Recovery Analysis of Percent Activation of Florisil

Caution must be taken not to overload the chromatographic columns. Column loading exceeding 30mg/g of adsorbent will cause a breakthrough of the interferences into the eluate. Concern for the loading of plant extracts are the species of lipids and chlorophyll. Chlorophyll and lipids are less problematic than oils, so to take the guideline of 30mg/g of adsorbent should be a good safeguard.

Table 2. Loading of Plant Extracts

Sample ID	Weight of Flask (g)	Weight of Flask + Sample (g)	Dry Weight of Sample (g)	Loading (mg/g)
LO-L-Q6-CF	17.3855	17.4585	1.8838	38.8
L-B-Q4-CF	17.3333	17.4347	1.7376	58.4

PAH standards and sample vegetation have been eluted through Florisil at 0, 5 and 10% deactivation to standardize the Florisil for the highest PAH recovery. All of the vegetation samples have been run through the Alumina to collect the base/neutral aromatics. The standards have been run separately for each column procedure.

Sample	Sample ID	Dry weight (g)	Percent Deactivation of Florisil (%)
2	LO-L-Q6-CF	5.7629	0
3	L-B-Q4-Cf	3.228	0
4	L-B-Q4-CF	5.7409	0
6	L-B-Q3-CF	4.3408	5
7	L-B-Q3-CF	5.2811	5
9	L-B-Q3-CF	4.7957	10

Each of the samples and stds are spiked with 100µL of 200 ppm deuterated standard. Each extract will be concentrated to 2 mL to give a final concentration of the standard of 10 ng/µL.

20µg in 100µL-- if final volume of 2 mL-- gives conc. of 10ng/µL

Verification of Plant Cleanup and Recoveries:

Verification Agenda

•Standard runs

1. run non-deuterated std (4µg/mL = 20µL of 200ppm Std, note the final concentration will be 2mL), through Florisil (0, 5,and 10% deactivation) in duplicate
   -at end of cleanup before making up to 1mL add deuterated std as an internal std (20µL of 200ppm Std)

2. run non-deuterated std (4µg/mL= 20µL of 200 ppm Std) through 5% Florisil and Alumina in duplicate

-add deuterated std as step 1 as internal std

3. run samples #2,3 and 4 with 0% deactivated Florisil + Alumina cleanup

4. run samples #6 and 7 with 5% deactivated Florisil + Alumina cleanup

5. run sample #9 with 10% deactivated Florisil + Alumina cleanup

note: for steps #3,4 and 5 a deuterated surrogate std (20µg in 100µL --final volume of 2mL--gives concentration of 10 µg/mL)

Samples	Naph.	Acen.	Phenan.	Chrysene	Perylene
0%-2veg	46	62	82	100	119
0%-3veg	59	77	83	88	101
0%-4veg	53	76	79	91	107
5%-6veg	50	71	61	59	95
5%-7veg	58	76	65	62	100
10%-9veg	59	78	64	62	92

Non-deuterated Standard Recoveries through Florisil at 0,5 and 10% Deactivation

Percent Florisil Deactivation

PAH	1-0%	%	3-5%	%	5-10%	%
Naphthalene	1.25	83.8	1.18	80.2	1.21	81
Acenaphthylene	1.21		1.12		1.16	
Acenaphthene	1.22	90.3	1.16	85.3	1.2	87
Fluorene	1.18		1.118		1.14	
Phenanthrene	1.13	94.3	1.103	89.9	1.05	88.7
Anthracene	1.09		1.09		1.027	
Fluoranthene	1.09		1.08		0.9787	
Pyrene	1.06		1.08		0.966	
Benz(a)anthracene	0.872		0.705		0.615	
Chrysene	0.877	103	0.751	96.9	0.723	105
Benzo(b)fluoranthene	0.739		0.501		0.541	
Benzo(k)fluoranthene						
Benzo(a)pyrene	0.5179		0.437		0.468	
Indeno(1,2,3-cd)	0.728		0.415		0.4708	
pyrene						
Dibenz(ah)	0.8013		0.435		0.404	
anthracene						
Benzo(ghi)perylene	0.708	104	0.427	88.2	0.477	95.2
Internal Standard						
Factor						
Naphthalene d-8	1.34		1.36		1.34	
Acenaphthene d-10	1.48		1.47		1.45	
Phenanthrene d-10	1.67		1.63		1.69	
Chrysene d-12	2.35		2.58		2.9	
Perylene d-12	2.95		4.13		3.99	

Reported Value Calculations

The calculations of the reported values was based on equations 1-5 as follows:

From the data of the GC-standard solution:

$$RFstd = \frac{\text{Peak height of STD}}{[STD]} \quad (1a)$$

$$RFIS = \frac{\text{Peak height of IS}}{[IS]} \quad (1b)$$

$$RRF = \frac{RFstd}{RFIS} = \frac{\text{Peak height of STD}}{[STD]} \times \frac{[IS]}{\text{Peak height of IS}} \quad (2)$$

Where

RFstd = response factor of compound added as standard or surrogate,

RFIS = response factor of compound added as internal standard,

RRF = relative response factor,

[STD] = concentration of compound added as standard or surrogate, and

[IS] = concentration of compound added as internal standard.

From the data of the sample solution,

$$[A] = \frac{[IS]}{RRF} \times \frac{\text{Peak height of A}}{\text{Peak height of IS}} \quad (3)$$

Where [A] = concentration fo analyte in sample solution.

Percentage recoveries are given by,

$$\% \text{ Recovery} = \frac{[A]}{[STD]} \times 100 \qquad (4)$$

The concentration in the original sample [A] SAMPLE can be known from,

$$[A]\ \text{sample} = [A] \times \frac{FV}{SV \text{ or } SW} \qquad (5)$$

Where

FV = final volume of the sample solution, and
SV or SW = volume or weight of the original sample.

Appendix B

Appendix B

For the PAH air analysis, the National Institute for Occupational Safety and Health Method 5515 was used. The adsorbent tubes- ORBO-43 were purchased from Supelco. To ensure the adsorbent tubes contained negligible interferences blanks were run. In addition the blanks were spiked to look at the extraction efficiency.

Table 1. Blank Extractions

Sample	Percent Recoveries				
	deuterated Naphthalene	deuterated Acenaphthalene	deuterated Phenanthrene	deuterated Chrysene	deuterated Perylene
	%	%	%	%	%
1-front section	67	72	98	137	87
1-back section	47	45	53	100	
2-front section	99	107	136	159	100
2-back section	98	108	136	157	99

note: to each blank 25µL of 200ppm deuterated std was added--5µg/5mL= 1µg/mL

Table 2. Air Sampler Calibration Data/Time/Volumes/Temperature (example)

Sample	Flow rate	Flow rate	Average	Sampling	dLF (display	Temp	Total
	Time - start	Time - end	Flow rate	Time (hrs)	low Flow	(o C)	Volume (L)
	mL/min	mL/min	L/min	(drun)	time)		
29-Jan	1692.79	1692.79	101.57	7.39	0.00	21	750.58
30-Jan	1569.77	1569.77	94.186	5.50	0.00	40	518.02

Once the analysis was completed as described in NIOSH Method 5515, instrumental analysis was performed on a Hewlett-Packard 5890 gas chromatograph coupled to a Hewlett-Packard 5970 mass selective detector.

Conversion from $\mu g/m^3$ to ppm was done by a conversion factor :

$$(x)\ \mu g/m^3 = \{(x)\ \text{x } 0.02445/\text{molecular weight }\}\ \text{ppm}$$

Appendix C

Level I Fugacity Model

Input Parameters

- Molecular weight (g/mol)
- Solubilty (g/m^3)
- Vapor pressure (Pa)
- Log K_{ow}

Physical-Chemical Properties of Selected PAHs

Physical-Chemical Properties	naphthalene	phenanthrene	chrysene	benzo(a)pyrene
Molecular Weight (g/mol)	128	178	228	252
Solubility (g/m^3)	31.7	1.29	0.002	0.0038
Vapor pressure (Pa)	10.4	0.0161	0.000085	0.0000007
Log K_{ow}	3.37	4.46	5.61	6.04

Fugacity f with units of pressure (Pa) is an equilibrium criterion which is related to concentration C ($mol.m^3$) through a fugacity capacity Z (mol/m^3Pa), where C = fZ. When two adjacent phases are at equilibrium, their fugacities are equal and partitioning can be described in terms of their Z values

$$C_1/C_2 = fZ_1/fZ_2 = Z_1/Z_2$$

The fugacity capacity of a chemical in a phase is dependent on the physical chemical properties of the compound as well as the environmental characteristics of the phase. A unique Z value exists for each chemical in each phase.

The plant model is constructed as illustrated schematically in Figure 1. Two bulk compartments, air and soil, surround the plant which consists of three compartments, roots, stem (including fruit or seeds) and foliage. The air compartment consists of two subcompartments of pure air and aerosol particles, and the soil consists of four subcompartments of air, water, organic and mineral matter.

The dimension of the illustrative plant which resemble those of a soybean at an intermediate stage of growth are summarized in Table 1.

Table 1. Dimensions of Illustrative Plant

Compartment	Volume (m^3)	Width (m)	Density (kg/m^3)
Roots	10×10^{-6}	-	830[a]
Stem	9.82×10^{-6}	0.005	830
Xylem	0.982×10^{-6}	0.00158	1000
Phloem	0.701×10^{-6}	-	1000
Leaf (20)	25×10^{-6}	5×10^{-4}	820

(a) Densities (o) were measured in our laboratories

The roots occupy a volume of 10 cm^3 or 10^{-5} m^3. The stem with a length 50 cm and a diameter of 0.5 cm has a volume of approximately 10 cm^3.

The foliage is considered to consist of 20 leaves with each individual leaf having a total area and thickness of 25 cm^2 and 0.5 mm respectively. This results in a total leaf volume of approximately 25 cm^3.

The fugacity capacities for air, water and soil are given in Table 2.

Table 2. Definitions and suggested Correlations for Z values (Pam^3/mol)

Compartment		
Air (Z_A)	1/RT	R = 8.314 (Pam^3/mol K) T = absolute temperature K
Air particles (Z_Q)	$Z_A K_{QA}$	K_{QA} = Aerosol-air partition coefficient
Water (Z_W)	1/H or C^s/P^s	H = Henry's Law constant (Pam^3/mol) C^s = aqueous solubility (mol/m^3) P^s = vapor pressure (Pa)
Soil (Z_E)	$xK_{OC}o_E Z_W$	K_{OC} = organic carbon partition coefficient = 0.41 Kow x = fraction organic carbon, *e.g.* 0.0015 o_E = soil density (kg/L)
Plant roots (Z_R)	RCF Z_W o_R/o_W	RCF = 0.82 + 0.014 K_{OW}
Plant stem (Z_S)	SXCF Z_X o_S/o_W	SXCF = 0.82 + 0.0065 K_{OW}
Plant xylem contents (Z_X)	1/H or Z_W, i.e. equivalent to water	
Plant phloem contents (Z_P)	1/H or Z_W, i.e. equivalent to water	
Plant leaf (Z_L)	$0.18Z_A + 0.80Z_W + 0.02 K_{OW} Z_W$, *i.e.* air, water, octanol "mixture"	
Densities (kg/L)	o_R = 0.83	o_E = 2.5
	o_S = 0.83	o_W = 1.0

$o_L = 0.82$

Note: o_W, o_X, o_R and o_S refers to densities of water, xylem sap, root and stem.

The first and simplest model describes a Level I or equilibrium distribution. No claim is made that equilibrium partitioning occurs in a real plant. The purpose of the calculation is merely to give an indication of the likely relative magnitudes of chemical amounts and concentrations in the plant. All compartments of the plant are assumed to achieve equilibrium with the external environment of soil or air, and thus have a common fugacity f (Pa). This fugacity cna be calculated from reported soil or air concentrations as f = Ci/Zi. It is then combined with individual Z values to calculate the concentration Ci.

Input to the model includes the properties of the chemical, including molecular weight (g/mol), vapor pressure (Pa), solubility (mol/m^3) and octanol/water partition coefficient, and the fugacity of the system.

Appendix D

D1 Methodology

The following routes of intake are considered for the dose estimates for humans at the Borradaile Site:

- ingestion of garden produce (*i.e.* both the leafy and the root vegetables);
- inhalation of suspended particles;
- ingestion of suspended particles from inhalation;
- ingestion of soil; and
- dermal exposure to contaminated soil.

D1.1 Dose Estimate for Ingestion of Garden Produce

The average daily dose for ingestion of garden produce is calculated by the following equation:

$$D_p = \frac{C_p\ Q\ F\ D\ B\ P}{A\ W}$$

where:

D_p = daily dose from ingested produce (mg/kg/day)
C_p = concentration of contaminant in produce (mg/kg)
Q = quantity of produce consumed (kg/day)
F = frequency of exposure (days/year)
D = number of years bounding exposure (years)
B = bioavailability of contaminant in produce (unitless)
P = fraction of produce grown on site
A = number of days bounding exposure (days)
W = body weight of receptor (kg)

The input values for the above equation are as follows:

C_p = site-specific values (see Section A1.1.1)

Q = 0.092 kg/day (adult) and 0.023 kg/day (child). The daily consumption of leafy vegetables for an adult is 0.046 kg/day (dry basis) (NRCC, 1979). The daily consumption of root vegetables is assumed to be 0.046 kg/day for an adult. The daily consumption of vegetables for a five year old child is assumed to be 25% of that of an adult.

F = 365 days/year

D = 70 years (adult) (U.S.EPA, 1986)
5 years (child) (U.S.EPA, 1989)

B = 1

P = 1

A = 70 years x 365 days/year = 2.56 x 10^4 days (adult)
5 years x 365 days/year = 1825 days (child)

W = 70 kg (adult) (NIOSH, 1980) and 16 kg (child). The weight of a child of five years old is assumed (U.S.EPA, 1989).

D1.1.1 Estimation of Concentration of PAH in Garden Produce

The concentration of contaminants in garden produce has to be estimated before the daily dose of contaminants from ingesting garden produce can be determined. The concentration of contaminants in garden produce can be estimated as follows:

$$C_p = C_f + C_r$$

where:

C_p = concentration of contaminants in garden produce (mg/kg)
C_f = the extent of contamination by contaminant from foliar deposition (mg/kg)
C_r = the uptake of contaminant from the soil via the roots (mg/kg)

D1.1.1.1 Extent of Contamination by Contaminant from Foliar Deposition

The extent of contamination from foliar deposition is estimated by the following equation:

$$C_f = d\ A_d$$

where:

C_f = the uptake of contaminant from foliar deposition (mg/kg)
d = deposition rate of contaminant (mg/m^2s)
A_d = leaf surface deposition factor (m^2s/kg)

D1.1.1.1.1 Deposition Rate

The deposition rate is defined by Hanna *et al.* (1982) as:

$$d = C_A\ V$$

where:

d = deposition rate (mg/m^2s)
C_A = ambient contaminant concentration in air near the surface (mg/m^3)
V = deposition velocity (m/s)

The deposition velocity is estimated by considering the following:

- the majority of PAH is adsorbed on particles in the atmosphere, 10 μm or less in diameter;
- for 10 μm diameter particles with density of 2.3 g/cm^3, the estimated deposition velocity is 0.007 m/s (Sehmel, 1980).

D1.1.1.1.2 Estimation of Leaf Surface Deposition Factor

The accumulation of contaminant by the plant from the deposition is not only dependent on the magnitude of the deposition rate but also on the leaf surface deposition factor.

The leaf surface deposition factor is dependent on factors such as the fraction intercepted by vegetation, crop yield and various chemically specific degradation processes.

The leaf surface deposition factor, A_d, can be estimated as follows (Holton *et al.*, 1984):

$$A_d = \frac{r[1 - exp(-\mathring{A}\ t)]}{Y\ \mathring{A}}$$

where:

A_d = leaf surface deposition factor (m^2s/kg)
r = interception fraction of plant (unitless)
$\mathring{A}$ = loss constant (s^{-1})
t = time of exposure of plant to atmospheric deposition (s)
Y = yield of the plant (kg/m^2)

The interception fraction is assumed to be 0.39 (Baes *et al.*, 1984). The loss constant is the sum of the losses due to weathering and volatilization:

$$\mathring{A} = K_w + K_v$$

The weathering rate constant is defined by:

$$K_w = \frac{0.693}{t_{1/2}}$$

where:

K_w = weathering rate costant (s-1)
$t_{1/2}$ = half-life of contaminant on the leaf due to washoff (s)

The half-life in air (in days) for benzo(a)pyrene and for chrysene is 6.0 and 5.5, respectively (U.S. EPA, 1986). There is no such information available for phenanthrene and naphthalene; a half-life of nine days is conservatively assumed.

The volatilization rate constant is defined by (Lyman *et al.*, 1982):

$$K_v = 509 \frac{[P_{vp}]}{[K_{oc}S]}$$

where:

K_v = volatilization rate constant (s^{-1})
P_{vp} = vapor pressure (mm Hg)
K_{oc} = the organic carbon-water partition coefficient (mL/g)

The period of exposure of the plant to atmospheric deposition is assumed to be the growing season, the duration of which is from June 1st to August 31st.

Crop yield was also considered because high crop yield has the effect of "diluting" the pollutant concentration in the plant by lowering the surface deposition factor. The yield of plant material as averaged from asparagus, broccoli, cabbage, cauliflower and lettuce is 2.61 kg/m^2 (U.S.EPA, 1978).

D1.1.1.2 Estimation of Uptake via Roots

The uptake of organic contaminants *via* roots can be estimated by the following equation:

$$C_r = C_s (U R_o)$$

where:

C_r = concentration of organic contaminant in plant due to uptake *via* roots (mg/kg)
UR_o = root uptake factor for an organic compound (unitless)
C_s = site specific concentration of contaminant in garden soil

D1.1.1.2.1 Root Uptake Factor

The root uptake factor for an organic compound is estimated by the following equation (Travis *et al.*, 1988):

$$log\ UR_o = 0.97 - 0.5\ (log\ K_{ow})$$

where:

UR_o = root uptake factor for an organic compound (unitless)
K_{ow} = octanol-water partition coefficient

D1.2 Dose Estimate for Inhalation of Suspended Particles

The average daily dose for inhalation is calculated by the following equation:

$$D_i = \frac{C_A\ Q\ F\ D\ B}{A\ W}$$

where:

D_i = daily dose from inhalation (mg/kg/day)
C_A = ambient contaminant concentration (mg/m^3)
Q = quantity of air inhaled daily (m^3/day or m^3/event)
F = frequency of exposure (days/year or events/year)
D = number of years bounding exposure (years)
B = bioavailability of contaminant (unitless)
A = number of days bounding exposure (days)
W = body weight of receptor (kg)

The input values for the above equation are as follows:

C_A = site specific value

Q = This estimation of Q for an adult of 23 m^3/day is based on eight hours of light activity requring 9.6 m^3 of air, eight hours of non-occupational activity requiring 9.6 m^3 of air, and eight hours of rest requiring 3.8 m^3 of air (ICRP, 1975). The quantity of air inhaled by a five year old child daily is estimated to be 16.8 m^3/day. This estimation of Q is based on 10 hours of light activity requiring 8 m^3 of air, 2 hours of moderate activity requiring 4 m^3 of air and 12 hours of rest requiring 4.8 m^3 of air (U.S.EPA, 1989).

For tilling, eight hours of moderate activity was assumed. For an adult, Q is 20 m^3/event and for a child, Q is 16 m^3/event.

F = 365 days/year for continuous exposure
5 events/year for tilling

D = 70 years (adult) and 5 years (child)

B = 0.25. It is assumed that 25% of inhaled matter are absorbed in the lower airways (U.S.EPA, 1983).

A = 70 years x 365 days/year = 2.56 x 10^4 days (adult) and 1825 days (child)

W = 70kg. The body weight of an adult male is assumed to be 70 kg (NIOSH, 1980). The body weight of a five year old child is assumed to be 16 kg.

D1.3 Dose Estimate for Ingestion of Suspended Particles Due to Inhalation

The input values for the dose estimate for ingestion suspected particles due to inhalation is assumed to be the same as the dose estimate for inhalation (Section A1.2)

D1.4 Dose Estimate for Ingestion of Soil

The average daily dose for ingestion of soil is calculated by the following equation:

$$D_S = \frac{C_S\ Q\ F\ D\ B}{A\ W}$$

where:

D_s = daily dose for ingestion of soil (mg/kg/day)
C_s = contaminant concentration in soil (mg/kg)
Q = quantity of soil ingested (kg/day)
F = frequency of exposure (days/year)
D = number of years bounding exposure (years)
B = bioavailability of contaminant (unitless)
A = number of days bounding exposure (days)
W = body weight of receptor (kg)

The input values for the dose estimate from ingestion of soil by humans are as follows:

C_s = site specific value

Q = 5×10^{-5} kg/day (adult) and 2×10^{-4} kg/day (children, 1 through 6 years) (U.S.EPA, 1989)

3×10^{-4} kg/day for gardening (adult) and 1.2×10^{-3} for gardening (child)*. The ingestion rate of soil during gardening is assumed to be six times the average daily ingestion rate.

5×10^{-4} kg/day for tilling (adult) and 2×10^{-3} kg/day for tilling (child)*. The ingestion rate of soil during tilling is assumed to be ten times the average daily ingestion rate.

*These values result from exposure in the area of the activity as against participation in the activity.

F = 240 days/year for the average rate of ingestion.
20 days/year for gardening.
5 days/year for tilling.

D = duration of lifetime exposure - 70 years (adult) and 5 years (child)

B = 0.5 (Paustenbach, 1989)

A = 365 days/years x 70 years = 2.56 x 10^4 days (adult) and 1825 (child)

W = 70 kg for adult male and 16 kg (child) (U.S.EPA, 1989).

D1.5 Dose Estimate for Dermal Exposure to Contaminated Soil

The average daily dose for dermal exposure to contaminated soil is calculated by the following equation:

$$D_S = \frac{C_S \, S \, A_b \, A_d \, F \, D}{A \, W}$$

where:

D_S = daily dose from dermal contact with soil (mg/kg/day)
C_S = contaminant concentration in soil (mg/kg)
S = skin surface area available for contact (m^2/event)
A_b = absorption factor (unitless)
A_d = soil to skin adherence factor (kg/m^2)
F = frequency of exposure (events/year)
D = number of years bounding exposure (years)
A = number of days bounding exposure (days)
W = body weight of receptor (kg)

The dermal exposure to contaminated soils can occur during both gardening and tilling. The children are exposed in the vicinity of the activity as against participation (as by adults) in the activity.

The input values for the above dose estimate due to gardening are as follows:

C_S = site specific value

S = 0.194 m^2/event (adult) and 0.073 m^2/event (child). 50th percentile total body surface (m^2) for an adult male is 1.94 (U.S.EPA, 1989). 50th

percentile total body surface (m^2) for a five year old child is 0.73 (U.S.EPA, 1989). 10% of the total body surface is assumed to be covered with soil during gardening.

A_b = 0.1. 10% of the contaminants in the soil on the body surface is assumed to be absorbed into the body.

A_d = 1.45×10^{-2} kg/m^2 (EPA, 1989). This value is based on the contact of hands with commercial potting soil.

F = 20 events/year

D = 70 years (adult) and 5 years (child)

A = 70 years x 365 days/year = 2.56×10^4 days (adult) and 1825 days (child)

W = 70 kg (adult) and 16 kg (child)

Dermal exposure to contaminated soils would be more severe during tillage operation. The input values for the above dose estimate due to tilling are the same as that for gardening except the following:

S = 0.97 m^2/event (adult) and 0.365 m^2/event (child). 50 percent of the total body surface is assumed to be covered with soil during tilling.

F = 5 events/year